HYBRIDIZATION AND DEPTH-RELATED EFFECTS OF SURFACE AND IMPURITY-LOCALIZED MODES IN FINITE TIGHT-BINDING CHAIN

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ABSTRACT. We deal with electronic states in a finite tight-binding chain of L atoms with two identical impurities, disposed symmetrically with respect to the midpoint of the chain at N lattice units from the surfaces. Symmetrical boundary conditions are assumed, the midpoint thus becoming the centre of symmetry; the normal electronic states (modes) of the system are then of two types: symmetric (S) and antisymmetric (A). Exact solutions of the eigenproblem are obtained and analytical conditions for the existence of localized states are established. We study the existence conditions for localized (impurity – IpM, as well as surface – SfM) modes in their dependence on three parameters: N – the distance between the surface and the impurity; a – the surface parameter; and c – the impurity parameter; the latter two are related with the surface and impurity potentials as follows: $V_{surface} = V_{bulk} - a$; $V_{impurity} = V_{bulk} - c$. Our analysis shows that the coexistence of the impurity and the surface affects their localization conditions differently: the surface condition is more highly sensitive to a deviation (from its bulk level) of the potential at the impurity (i.e. to the impurity parameter c) than to the distance N between the surface and the impurity, whereas the impurity condition is primarily sensitive to the distance N and moreover – for antisymmetric mode – to the impurity-midpoint distance, but less sensitive to the surface parameter a. The dependence of the localization conditions on the location N of the impurity in the chain is formulated and expressed in the form of a "surface-midpoint co-action rule": A tendency of the impurity to move towards the surface causes delocalization of both impurity modes (S and A) localized thereon, whereas its motion towards the centre delocalizes the mode A only, at the same time strongly enhancing the localization of the mode S. In particular it follows from this rule that the emergence of localized modes can be provoked solely by the process of "immersion" of the impurity into the bulk of the chain.

The parameters a and c act competitively: an increase in a tends to localize the mode on the surface, whereas an increase in c tends to localize it at the impurity. Moreover, if both parameters become sufficiently strong, coexistence of surface- and impurity-localized modes is achieved. The particular regions corresponding to their coexistence are determined both in the a-c plane and the N-c plane. It is shown that if a pair of modes of the same symmetry – one impurity-localized and the other surface-localized – coexist, they may hybridize under certain conditions. Impurity-surface hybridization can be achieved by varying a or c (with N maintained constant) as well as by changing the location N of the impurity in the chain, with the parameters a and c constant. All possible hybridization effects are reviewed and discussed in detail.

Moreover, the effects of impurity-surface interaction are visualized by the introduction of the concept of effective length of the chain. The impurity, when deep in the chain, "feels" specifically the

changes occurring at its ends: it "perceives" how a perturbation "a" of the surface modifies effectively the length of the chain, shifting either of the "unperturbed" ends by an amount $a/(1-a)$. Depending on the value of a, this can lead to a lengthening or shortening of the chain, i.e., to weaker or enhanced influence of the "perturbed" surface on the impurity.

In our work we have restricted ourselves to the case of one-electron stationary states of a finite one-dimensional lattice. However, the same mathematics are applicable as well to other problems of a finite quantum chain, e.g., to those of a single phonon, magnon or hole. One may also consider the extension of our model to three dimensions (e.g., thin films and superlattices).

Notations

a – the surface parameter
c – the impurity parameter
E – reduced mode energy
k – the wave number of a bulk mode
l – number labelling the position of an atom in the chain
L – the number of atoms in the chain
n – number labelling the mode (running from the energetically lowest one)
N – the distance of the impurity from the surface (in lattice units)
t – the localization increment of a localized mode
Δ – the distance of the impurity from the centre of the chain (in lattice units)
u_l – mode amplitude

Abbreviations

A – antisymmetric
BEM – band-edge mode (top or bottom)
BM – bulk mode
Ip – impurity
IpM – impurity-localized mode
LA (LB) – localized mode, whose energy lies above (below) the bulk band
S – symmetric
Sf – surface
SfM – surface-localized mode

1. THE MODEL

It is only within the last few years that the problem of how the distance from the surface of an impurity in the bulk affects the surface electronic properties has attracted attention [1, 2]. Ueba [1] considered a semi-infinite linear chain containing an impurity in its bulk and found that the surface state energy depends both on the location of the impurity atom with regard to the surface as well as on the impurity potential. Sulston et al. [2] also studied a semi-infinite chain of atoms containing an impurity atom at some distance from the surface in order to calculate how the the presence of an impurity substantially affects the metal chemisorption properties.

It is a well known fact that the surface of a crystal constitutes by itself a structure defect at which, under certain conditions, surface-localized electronic states appear [3–5]. On the other hand, it is also well known that if an impurity atom is located in the bulk of a crystal, impurity-localized states arise [6]. It is the aim of the present work to study the problem of coexistence of these two types of localized states in a finite one-dimensional crystal (a chain) containing two impurity atoms, symmetrically disposed with respect to the centre of the chain. In particular, we are interested in elucidating the effects exerted on the electronic energy spectrum of the chain if one shifts the impurities progressively from the ends of the chain (surfaces) towards the centre of the chain (midpoint).

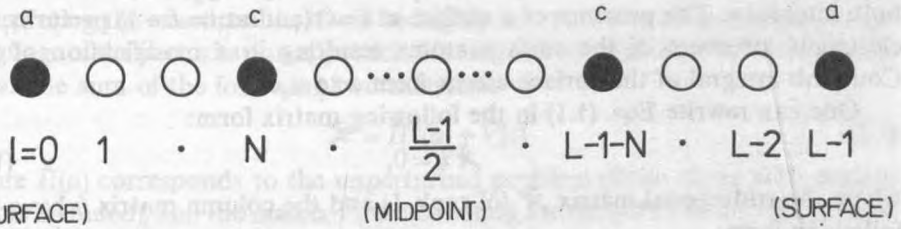


Fig 1.1. Diagram equivalent to the orbital model of a finite chain of atoms, with two impurities located symmetrically with respect to the chain centre (midpoint) at positions $l=N$ and $l=L-1-N$. The quantities a and c are, respectively, surface and impurity (diagonal) perturbation parameters (defined in the text) describing the deviation from the unperturbed bulk potential. All resonance integrals between the chain atoms are assumed to be the same.

In what follows, we shall proceed within the framework of the tight-binding model. We follow the formulation of the surface problem of Davison and Levine [4], while the impurity problem is described by the Koster-Slater [7] and Grimley [8] schemes. We shall consider a finite chain consisting of the following L atoms (labelled $l=0, 1, 2, \ldots, L-1$; see Fig. 1.1): two boundary (surface) atoms ($l=0; L-1$), two impurity atoms ($l=N; L-1-N$) and the remaining $L-4$ bulk-host atoms. If it happens that an electron is localized on the boundary (impurity) atom, the corresponding state will be referred to as a surface (impurity) state. We write the equations of motion of an electron in the one-dimensional finite crystal in the form of a set of difference equations:

$$
\begin{aligned}
&(\tilde{E}-\alpha_1)u_0-\beta u_1=0, && l=0\\
&-\beta u_0+(\tilde{E}-\alpha)u_1-\beta u_2=0, && l=1\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
&-\beta u_{N-1}+(\tilde{E}-\alpha_2)u_N-\beta u_{N+1}=0, && l=N\\
&-\beta u_{l-1}+(\tilde{E}-\alpha)u_l-\beta u_{l+1}=0, && l=N+1, \ldots, L-2-N\\
&-\beta u_{L-2-N}+(\tilde{E}-\alpha_2)u_{L-1-N}-\beta u_{L-N}=0, && l=L-1-N\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots
\end{aligned}
$$

$$-\beta u_{L-3}+(\tilde{E}-\alpha)u_{L-2}-\beta u_{L-1}=0, \qquad l=L-2$$
$$-\beta u_{L-2}+(\tilde{E}-\alpha_1)u_{L-1}=0, \qquad l=L-1 \tag{1.1}$$

where the notations used have the standard meaning: α and β denote the Coulomb and resonance integrals, respectively, $\tilde{E}$ is the energy of the electron and $u_l \equiv u_l(k)$ is a coefficient of the expansion of the electron wave function in a linear combination of atomic orbitals. In Eqs. (1.1) only those terms which represent interaction between nearest-neighbour atoms are retained. The impurity atoms are incorporated into the system from the very beginning. The difference between their electronic structure and that of the bulk atoms is taken into account by introducing in Eqs. (1.1) the impurity Coulomb integral α_2, different from the bulk integral α. The presence of a surface at $l=0$ (and at $l=L-1$) perturbs the electronic structure of the surface atoms resulting in a modification of the Coulomb integral of the surface atoms from α to α_1.

One can rewrite Eqs. (1.1) in the following matrix form:

$$\check{\mathcal{H}}\check{u}=0, \tag{1.2}$$

where the tridiagonal matrix $\check{\mathcal{H}}$ (of rank L) and the column matrix $\check{u}$ have the following form:

$$\check{\mathcal{H}}=\begin{bmatrix} x-a, & -1 & & & & & & & & \\ -1, & x, & -1 & & & & & & & \\ & \cdots & \cdots & \cdots & & & & & & \\ & & -1, & x, & -1 & & & & & \\ & & & -1, & x-c, & -1 & & & & \\ & & & & -1, & x, & -1 & & & \\ & & & & & \cdots & \cdots & \cdots & & \\ & & & & & & -1, & x, & -1 & \\ & & & & & & & -1, & x-c, & -1 \\ & & & & & & & & -1, & x, & -1 \\ & & & & & & & & & \cdots & \cdots \\ & & & & & & & & & & -1, \quad x-a \end{bmatrix}_L ; \quad \check{u}=\begin{bmatrix} u_0 \\ u_1 \\ \cdot \\ u_{N-1} \\ u_N \\ u_{N+1} \\ \cdot \\ u_{L-2-N} \\ u_{L-1-N} \\ u_{L-N} \\ \cdot \\ u_{L-1} \end{bmatrix}_L \tag{1.3}$$

The new notations used here are the following:

$$x=\frac{\tilde{E}-\alpha}{\beta}, \quad a=\frac{\alpha_1-\alpha}{\beta}, \quad c=\frac{\alpha_2-\alpha}{\beta}. \tag{1.4}$$

The dimensionless quantity (the reduced energy)

$$E=-\tfrac{1}{2}x \tag{1.4a}$$

will be simply referred to henceforth as the "energy". The physical meaning attached to the perturbation parameters a and c is the following: since the

quantity β is assumed to be negative, $-a$ and $-c$ are directly related to the difference between the atomic potentials experienced respectively by the surface/impurity atom and the bulk host atoms. Therefore a positive value of the perturbation parameter corresponds to the potential well, whereas a negative value to the potential barrier. In the following we shall refer to the perturbation parameters as follows: a – surface parameter, and c – impurity parameter. Since the position of one impurity determines univocally the position of the other impurity owing to the symmetry requirement, we shall henceforth describe our "two-impurity system" in terms of the location of one impurity only.

Our eigenproblem (1.2.) will be solved exactly in Section 3, where the eigenfunctions and eigenvalues will be presented in closed form. However, when interpreting the exact results, it will be highly instructive to have recourse to the language of the perturbation approach. Having this in mind we rewrite the matrix $\check{\mathscr{H}}$ as the sum of the following two matrices:

$$\check{\mathscr{H}} = \check{H}^0(a) + \check{V}(c) \tag{1.5}$$

where $\check{H}(a)$ corresponds to the unperturbed problem (finite chain with surface effects included), and the matrix $\check{V}(c)$ accounting for the perturbation introduced by the impurity. Obviously, the matrix $\check{V}(c)$ has but two nonzero elements: these are $V_{NN} = V_{L-1-N;L-1-N} = -c$. In the first approximation of classical perturbation calculus the perturbation in energy of the level E_n^0 amounts to

$$\Delta E_n^{(1)} \equiv E - E_n^0 = V_{nn} = -2c\,|u_N(E_n^0)|^2 \tag{1.6}$$

where $u_N(E_n^0)$ is the unperturbed amplitude of the wave function at the node to be invested with the impurity ($l = N$). The second-order perturbation contributed by the state $E_{n'}^0$ to the energy of the level E_n^0 amounts to

$$\Delta E_n^{(2)} = \frac{|V_{nn'}|^2}{E_n^0 - E_{n'}^0}. \tag{1.7}$$

If the states n and n' differ in symmetry (the one is symmetric and the other antisymmetric) the matrix element is identically equal to zero and the second-order correction contributes nothing to the energy. If, however, the two states possess the same symmetry, this correction is nonzero, amounting to

$$\Delta E_n^{(2)} = \frac{4c^2}{E_n^0 - E_{n'}^0} |u_N(E_n^0)|^2 |u_N(E_{n'}^0)|^2. \tag{1.8}$$

Thus, an impurity introduced into the system perturbs the energy levels of the latter. The magnitude of the perturbation is dependent both on its properties as given by the parameter c and on the pre-existing properties of the unperturbed system given by the squared amplitude of the unperturbed wave functions at the node occupied by the impurity. The sign of the first-order perturbation is always opposite to that of the impurity parameter; as to magnitude, it is proportional to the latter. The second-order perturbation is, as to its sign, dependent on the

mutual disposition of the interacting levels and is inversely proportional to their difference and directly proportional to the square of the impurity parameter. Obviously, we keep in mind that states of different symmetry do not interact mutually and since the nearest neighbours of each energy level in the unperturbed system (both from above and from below) are levels of opposite symmetry, the second-order correlations from more remote levels of the same symmetry contribute but insignificantly to the energy of the level under consideration. However, an exceptional situation can arise: if two closest lying levels with the same symmetry are localized modes, and if the perturbation is appropriately great, the two levels can come sufficiently close to each other (due to the first-order correction) for the second-order effects to become perceptible. As we know, the levels then begin to exert a repulsive action mutually and, in the intermediate (crossover) region, a hybrid of the two localized modes arises.

Moreover, from the preceding formulae, the perturbation (first- and second-order) of a given level due to the presence of the impurity is dependent only on the amplitudes of the unperturbed wave functions at those modes which harbour an impurity. We can thus expect the eigen-energies of our initial problem to be "sensitive" to the position of the impurity in the chain i.e. to be functions of the parameter N, thus $E_n = E_n(N)$. Obviously, for the same reasons, the eigenfunctions corresponding to these energies will also be impurity-position sensitive. Our work will be largely devoted to a study of the effects accompanying changes in the position N of the impurity along the chain.

2. CONCEPTS AND TERMINOLOGY

A chain of a given number L of atoms will be said to possess a well defined spatial structure if the location N of an impurity in the chain is determined exactly. If, however, only the value of the two (surface a and impurity c) parameters are well determined, the chain will be said to possess a prescribed potential structure only. The eigen-vibration problem of the chain is completely determined if the two structures of the chain (its spatial and potential structure) are prescribed simultaneously. The particular case of potential structure with $c=0$ will be referred to as that of an impurity-less chain; the latter is then characterized by the two parameters L and a only. If, however, $a=0$ (denoting an unperturbed surface potential) the complete structure of the chain is determined by three parameters L, N and c; this case will be referred to briefly as that of "unperturbed surface".

We now introduce the concept of a mental process whereby the location N of the impurity undergoes a change leaving the other structural parameters of the chain unchanged. In fact, this amounts to considering a set of chains (see Fig. 2.1), with impurity location N increasing progressively by unity from one chain to the next. The process will be referred to as an $N\uparrow$-process if N grows (that is, if the

distance of the impurity from the surface increases) and as an $N\downarrow$-process if N decreases (if the impurity "moves away" from the centre of the chain). We shall be studying how the energy of the individual eigen-modes of the chain varies in the course of the N-process. The graph of the energy of a given state versus the location N of the impurity in the chain will be referred to as the E-N pattern of the state or, briefly, its "energy-pattern". The energy-pattern will be shown to exhibit certain characteristic properties: it is oscillatory in the case of bulk states and monotonous in that of localized states. Moreover, the energy-pattern of localized states will be shown to reveal the existence of two effects, cooperating in the N-process: the one residing in a "freeing" of the impurity from the influence of the surface ("surface effect", predominant in the range of small N), and the other residing in the progressive subjection of the impurity to the influence of the centre of the chain ("midpoint effect", in the range of great N).

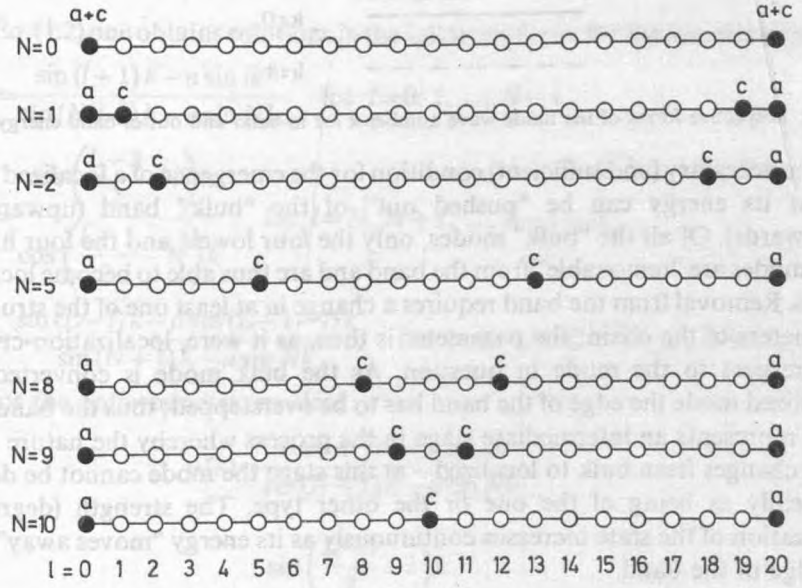


Fig 2.1. Set of chains with impurity location N increasing progressively by unity from one chain to the next; a – the surface parameter, c – the impurity parameter.

Modes with energy in the permitted band are of the bulk type: their amplitude varies oscillatorily along the chain. Modes with an energy lying outside (above or below) the permitted band (see Fig. 2.2) are of the nature of localized states, i.e., of ones with an amplitude decreasing monotonically away from the region of their localization. With regard to their localization region, we divide localized states into two types: surface-localized, and impurity-localized according to which of the two amplitudes (surface or impurity) is greater. Further on, however, we shall

show that the type of localization of a given mode can change as the result of a change in the structural parameters of the chain.

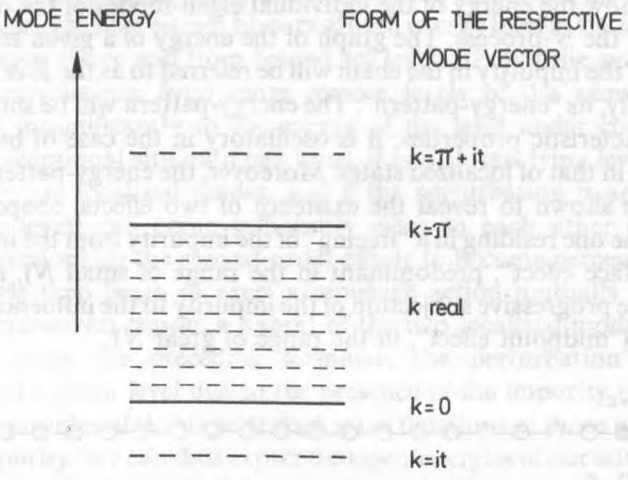


Fig 2.2. Respective forms of the mode wave number k for in-band and out-of-band energy levels.

The necessary (and sufficient) condition for the emergence of a localized mode is that its energy can be "pushed out" of the "bulk" band (upwards or downwards). Of all the "bulk" modes, only the four lowest and the four highest lying modes are "removable" from the band and are thus able to become localized modes. Removal from the band requires a change in at least one of the structural parameters of the chain; the parameter is then, as it were, localization-creative with respect to the mode in question. As the bulk mode is converted into a localized mode the edge of the band has to be overstepped; thus the band-edge mode represents an intermediate stage in the process whereby the nature of the mode changes from bulk to localized – at this stage the mode cannot be defined univocally as being of the one or the other type. The strength (degree) of localization of the state increases continuously as its energy "moves away" from the edge of the band.

Quite generally, the maximal number of localized modes in coexistence is equal to that of the spatial perturbations present in the system. In the chain under consideration by us, this number amounts to four (two surfaces and two impurities). A given perturbation can be "occupied" by one localized mode only. Whenever a localized mode is created, i.e., whenever its energy oversteps the edge of the band, the essential question is whether other localized modes already exist in the system; if so, it is created under conditions in which some of the perturbations are already "occupied". Now, since localized modes are generally created in pairs (one symmetric mode and one antisymmetric mode), we shall refer to the pair that is the first to detach itself from the band as primary modes

and to the pair that detaches itself next – as secondary modes. Whereas the former are quite free to chose the perturbations they will occupy (since all the perturbations are still unoccupied), the latter are restricted in their choice (since some of the perturbations are already occupied).

All the numerical results given below have been obtained on the assumption of $L=21$. We restrict ourselves to the study of LB modes only (unless specified otherwise). IpM modes are marked with full circles, SfM modes – with void circles.

3. THE EIGENPROBLEM. LOCALIZED MODES

Due to the symmetricity of the boundary and impurity conditions of our chain (see Eqs. (1.3)), the eigensolutions of Eq. (1.2) represent modes of only two types, namely: symmetric and antisymmetric. On insertion of

$$x=2\cos k \tag{3.1}$$

into Eq. (1.2) one obtains solutions in the following form: for the symmetric modes:

$$u_l(k)=\frac{\sin(l+1)k-a\sin lk}{\sin(N+1)k-a\sin Nk} \quad \text{for } l=0, 1, \ldots, N-1$$

$$u_l(k)=\frac{\cos\left(\frac{L-1}{2}-l\right)k}{\cos\left(\frac{L-1}{2}-N\right)k} \quad \text{for } l=N, N+1, \ldots, L-1-N$$

$$u_l(k)=\frac{\sin(L-l)k-a\sin(L-1-l)k}{\sin(N+1)k-a\sin Nk} \quad \text{for } l=L-N, L-N+1, \ldots, L-1; \tag{3.2a}$$

and for the antisymmetric modes:

$$u_l(k)=\frac{\sin(l+1)k-a\sin lk}{\sin(N+1)k-a\sin Nk},$$

$$u_l(k)=\frac{\sin\left(\frac{L-1}{2}-l\right)k}{\sin\left(\frac{L-1}{2}-N\right)k},$$

$$u_l(k)=-\frac{\sin(L-l)k-a\sin(L-1-l)}{\sin(N+1)k-a\sin Nk}. \tag{3.2b}$$

These solutions have still to be normalized. This will be done numerically further on.

The wave number k can only take values permitted by the following characteristic equations:

$$2\cos k - c - \frac{\sin Nk - a\sin(N-1)k}{\sin(N+1)k - a\sin Nk} =$$

$$= \begin{cases} \dfrac{\cos\left(\dfrac{L-3}{2} - N\right)k}{\cos\left(\dfrac{L-1}{2} - N\right)k} & \text{for the symmetric modes,} \quad (3.3a) \\[2ex] \dfrac{\sin\left(\dfrac{L-3}{2} - N\right)k}{\sin\left(\dfrac{L-1}{2} - N\right)k} & \text{for the antisymmetric modes.} \quad (3.3b) \end{cases}$$

These two equations lead jointly to L allowed values of the variable k. The set of these values is obviously dependent on the chain length L, the location N of the impurity, and the two perturbation parameters involved: the surface parameter a and the impurity parameter c.

Localized modes correspond to complex k: in particular, if $k = it$ ($t > 0$), the corresponding mode energy lies below the bulk band, whereas if $k = \pi + it$ the respective energy level lies above the bulk band. Depending on the mutual relations holding between the perturbation parameters a, c and N, these states can be localized on the impurity layers, or can be surface-localized. In order to establish the existence conditions for the localized modes in general, we start by writing down the existence conditions for modes corresponding to the edges of the band, namely, the existence conditions for the mode $k = 0$ (lower band edge) and for the mode $k = \pi$ (upper band edge). These conditions result from Eqs. (3.3) on insertion therein of $k = 0$ or $k = \pi$, respectively. For the mode $k = 0$ we obtain the following equations: for the symmetric mode

$$\left(a - \frac{N+1}{N}\right)\left(c - \frac{1}{N}\right) = \left(\frac{1}{N}\right)^2, \quad (3.4a)$$

and for the antisymmetric mode

$$\left(a - \frac{N+1}{N}\right)\left(c - \frac{1}{N} - \frac{2}{L-1-2N}\right) = \left(\frac{1}{N}\right)^2. \quad (3.4b)$$

To obtain the existence conditions of the mode $k = \pi$ we only need to replace a and c by $-a$ and $-c$ in Eqs. (3.4). The hyperbolae (3.4) divide the $c-a$ plane into regions in which the respective localized mode does exist, or does not exist. This is shown in Fig. 3.1, where each region is characterized by a symbol (mS, nA), meaning that m symmetric localized modes and n antisymmetric localized modes exist in it. Therefore, the Figure provides information regarding

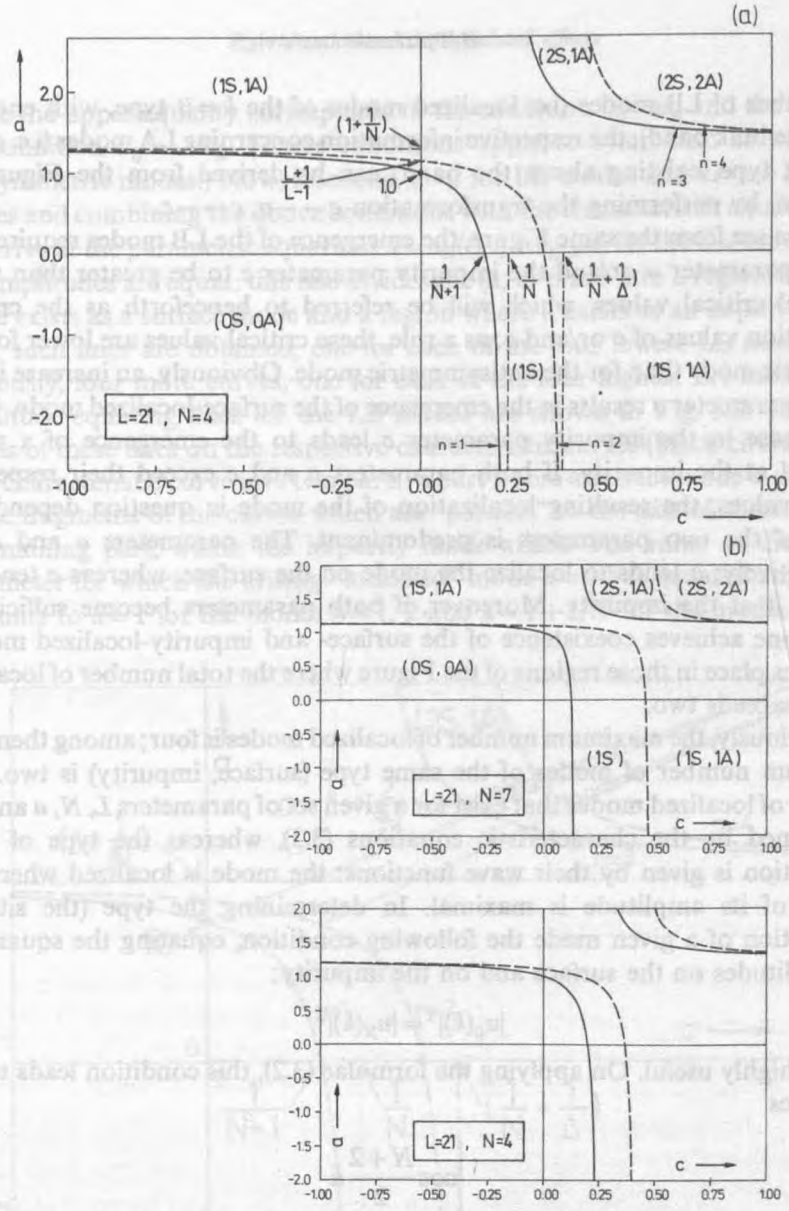


Fig 3.1. Existence conditions for LB modes in a chain consisting of L atoms, with two identical impurities symmetrically disposed (with regard to the chain centre) at a distance of N lattice units from either surface of the chain. The solid curves correspond to the existence conditions for the symmetric $k=0$ mode, whereas the dashed curves – to those of the antisymmetric $k=0$ mode. The hyperbolae are boundaries at which localized modes emerge; therefore these curves split the c-a plane into regions, each labelled by a symbol (mS, nA), in which respectively m symmetric and n antisymmetric localized modes exist simultaneously. Notations: a – the surface parameter, c – the impurity parameter, and $\Delta=(L-1)/2-N$ the distance of the impurity from the chain center.
(a) general overview;
(b) comparison of the two cases corresponding to $N=4$ and $N=7$.

the number of LB modes (i.e. localized modes of the $k=it$ type, with energies below the bulk band); the respective information concerning LA modes (i.e. of the $k=\pi+it$ type, existing above the band) can be derived from the Figure on reflection, by performing the transformation $a\rightarrow -a$, $c\rightarrow -c$.

As we see from the same Figure, the emergence of the LB modes requires the surface parameter a or/and the impurity parameter c to be greater than some (positive) critical values, which will be referred to henceforth as the critical localization values of a or/and c; as a rule, these critical values are lower for the symmetric mode than for the antisymmetric mode. Obviously, an increase in the surface parameter a results in the emergence of the surface-localized mode, while an increase in the impurity parameter c leads to the emergence of a mode localized at the impurity. If both parameters a and c exceed their respective critical values, the resulting localization of the mode in question depends on which of the two parameters is predominant. The parameters a and c act competitively; a tends to localize the mode on the surface, whereas c tends to localize it at the impurity. Moreover, if both parameters become sufficiently strong one achieves coexistence of the surface- and impurity-localized modes; this takes place in those regions of the Figure where the total number of localized modes exceeds two.

Obviously, the maximum number of localized modes is four; among them, the maximum number of modes of the same type (surface, impurity) is two. The number of localized modes that exist for a given set of parameters L, N, a and c is determined by the characteristic equations (3.3), whereas the type of their localization is given by their wave functions: the mode is localized where the square of its amplitude is maximal. In determining the type (the site) of localization of a given mode the following condition, equating the squares of its amplitudes on the surface and on the impurity:

$$|u_0(k)|^2=|u_N(k)|^2 \tag{3.5}$$

proves highly useful. On applying the formulae (3.2), this condition leads to the equalities

$$a=\begin{cases} \dfrac{\cos\dfrac{N+2}{2}k}{\cos\dfrac{N}{2}k} & (3.6a) \\[2ex] \dfrac{\sin\dfrac{N+2}{2}k}{\sin\dfrac{N}{2}k}, & (3.6b) \end{cases}$$

where the upper equality corresponds to the condition $u_0 = u_N$ and the lower to the condition $u_0 = -u_N$. (These conditions apply to symmetric as well as to antisymmetric modes.) Now, inserting $k = it$ for LB modes and $k = \pi + it$ for LA modes and combining the above conditions with the characteristic equation (3.3) we arrive at the parametric equations $a = a_N(t)$, $c = c_{L,N}(t)$ for the line along which the amplitudes are equal: this line divides the (a, c)-plane into a region where the mode exists as a surface mode and a region where it exists as an impurity mode. Four such lines are obtained, one for each of the four lowest LB modes (and, obviously, four more curves, one for each of the four highest LA modes). The amplitude-equating lines for the LB modes are shown in Fig. 3.2. The initial points of these lines on the respective characteristic curves (black circles) divide each characteristic curve into two parts: a part where a surface mode is generated (those fragments of the curves which are "parallel" to the axis of abscissae) and a remaining part, where the impurity mode arises. The value of the surface parameter for which the arising "localized" mode $k = 0$ has equated amplitudes amounts to $a = 1$ for the modes $n = 1, 2$ and $a = 1 + 2/N$ for the modes $n = 3, 4$.

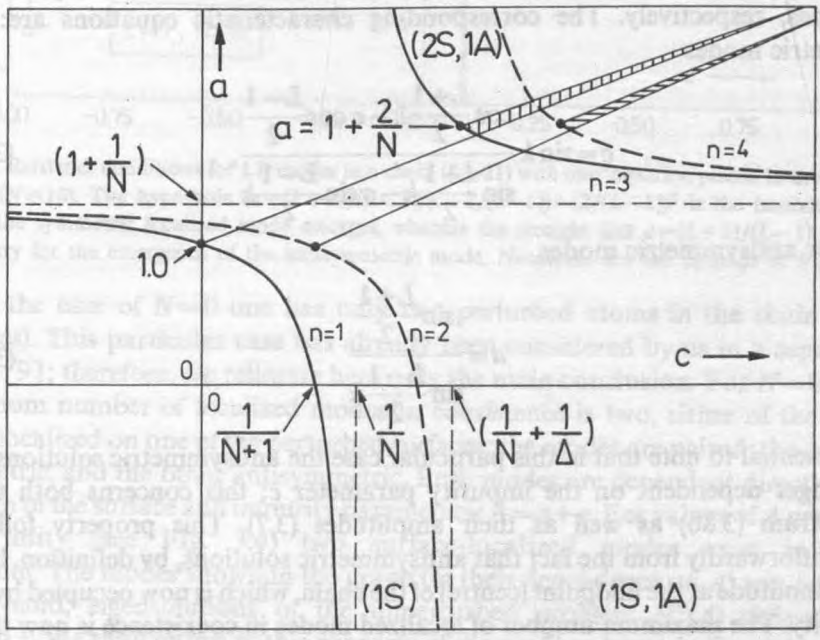


Fig 3.2. The shaded regions show schematically the swapping regions for symmetric modes ($n = 1$, 2 – upper region) and antisymmetric modes ($n = 3$, 4 – lower region). They are bounded by lines of equal surface and impurity amplitudes. These lines originate in points with $a = 1$ for the modes $n = 1$, 2 and with $a = 1 + 2/N$ for the modes $n = 3, 4$. At high values of a and c the swapping regions overlap, since all the iso-amplitude lines then coalesce into a single line.

We shall now discuss the influence of the location N of the impurity on the existence conditions of localized modes. To facilitate the discussion we first consider two extreme cases, namely the case when the impurity is in the centre of the chain (i.e., $N=(L-1)/2$, midpoint), and the other extreme case when the impurity is on the surface (i.e., $N=0$).

The eigenmodes for the case $N=(L-1)/2$ are given by the following formulae (with normalization constant omitted):

$$u_l(k)=\sin(l+1)k-a\sin lk, \quad \text{for } l=0,1,\ldots,\frac{L-3}{2}$$

$$u_{(L-1/2)}(k)=\begin{cases}\sin\dfrac{L+1}{2}k-a\sin\dfrac{L-1}{2}, & \text{for symmetric modes}\\ 0 & \text{for antisymmetric modes}\end{cases}$$

$$u_l(k) =\pm[\sin(L-l)k-a\sin(L-1-l)k], \quad \text{for } l=\frac{L+1}{2},\ldots,L-1; \tag{3.7}$$

in the last formula the signs $\pm$ correspond to symmetric and antisymmetric solutions, respectively. The corresponding characteristic equations are: for symmetric modes

$$c=\sin k\,\frac{\cos\dfrac{L+1}{2}k-a\cos\dfrac{L-1}{2}}{\sin\dfrac{L+1}{2}k-a\sin\dfrac{L-1}{2}k}, \tag{3.8a}$$

and for antisymmetric modes

$$a=\frac{\sin\dfrac{L+1}{2}}{\sin\dfrac{L-1}{2}k} \tag{3.8b}$$

It is essential to note that in this particular case the antisymmetric solutions are no longer dependent on the impurity parameter c; this concerns both their k-spectrum (3.8b) as well as their amplitudes (3.7). This property follows straightforwardly from the fact that antisymmetric solutions, by definition, have zero amplitude at the midpoint (centre) of the chain, which is now occupied by the impurity. The maximum number of localized modes in coexistence is now three (see Fig. 3.3), obviously corresponding to the three "perturbed atoms" present in the system (two surfaces, one impurity). Two of the three modes form a pair, consisting of one symmetric and one antisymmetric mode, and are surface-localized; the remaining third mode is the impurity-localized symmetric mode. We thus formulate the following, general rule: One has no possibility of provoking the

existence of the impurity-localized antisymmetric mode if the impurity constitutes the centre of symmetry (the midpoint). This rule explains why, when working on impurity problems of bulk samples (such problems are naturally symmetrical), one obtains only one impurity-localized symmetric mode.

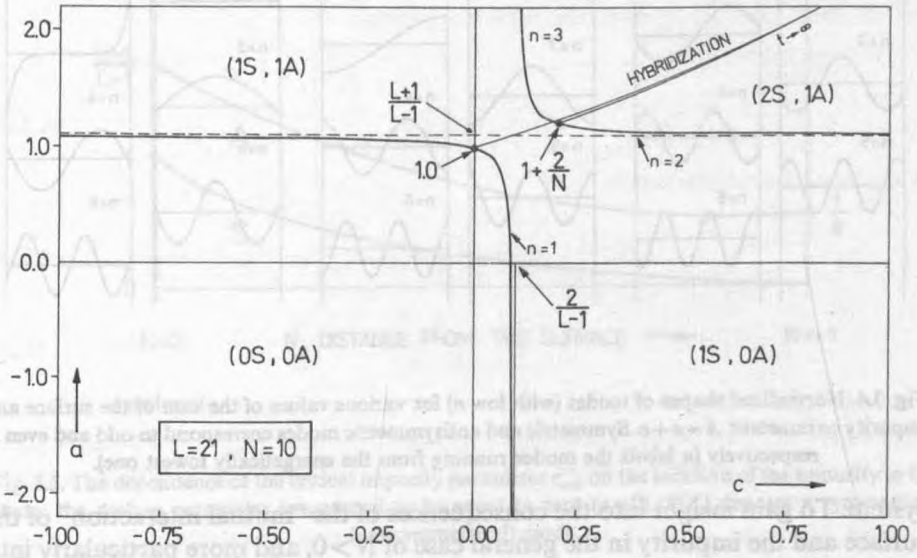


Fig 3.3. Existence conditions for LB modes in a chain ($L=21$) with one impurity, placed in the chain centre ($N=10$). The hyperbola $(a-(L+1)/(L-1))(c-2/(L-1))=(2/(L-1))^2$ is the boundary at which the symmetric localized mode emerges, whereas the straight line $a=(L+1)/(L-1)$ is the boundary for the emergence of the antisymmetric mode. Notations are the same as in Fig. 3.1.

In the case of $N=0$ one has only two perturbed atoms in the chain (the surfaces). This particular case has already been considered by us in a separate paper [9]; therefore, we reiterate here only the main conclusion. For $N=0$, the maximum number of localized modes in coexistence is two, either of the two being localized on one of the perturbed surfaces; the modes are paired: the one is symmetric, and the other antisymmetric. Both modes are dependent directly on the sum of the surface and impurity parameters: $A=a+c$. For values of A greater than unity (see Fig. 3.4) two surface-localized modes exist in the spectrum. The modes shown in the graph (in their dependence on A) are, on the other hand, eigensolutions of the unperturbed problem $\hat{H}^0(A)$ defined in Section 1. We shall return to this property of the profiles shown in Fig. 3.4 in the further sections of this paper.

The case of $N=1$ also has already been considered in a separate paper [10]. In this case two surface and two sub-surface localized states can coexist; their respective localization conditions (involving both surface and sub-surface parameters) express mutual "interaction" of the two perturbations present in the

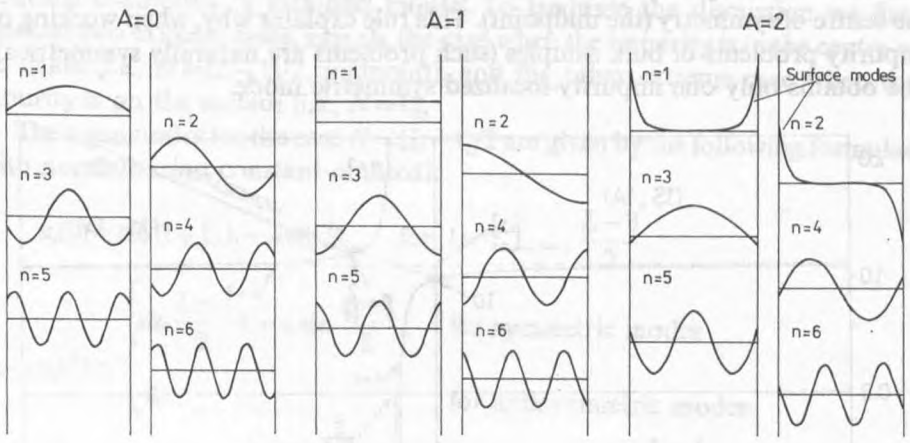


Fig. 3.4. Normalized shapes of modes (with low n) for various values of the sum of the surface and impurity parameters: $A=a+c$. Symmetric and antisymmetric modes correspond to odd and even n, respectively (n labels the modes running from the energetically lowest one).

system. To gain insight into the consequences of the "mutual interaction" of the surface and the impurity in the general case of $N>0$, and more particularly into the manner in which their presence affects the critical conditions determining the emergence of the localized modes, we shall now consider the situation when $a=0$, i.e., when the Coulomb integral on the surface is unmodified but all bonds extending out of the surface are cut. The critical impurity parameter for the symmetric mode now amounts to $c_{crit}=1/(N+1)$ (it will be kept in mind that N is the distance from the impurity to the surface). It hence results that if the impurity "moves" nearer and nearer to the surface it becomes increasingly difficult to generate a localized mode on the impurity because c_{crit} increases; if the impurity "moves away" from the surface the inverse occurs; and in the extremal case of $N\to\infty$ we get the condition $c_{crit}=0$, the impurity becomes endowed with the properties of a "bulk impurity". Note that if the impurity is on the surface ($N=0$) we get the critical condition for the arisal of a surface mode $c\to a$, $a_{crit}=1$. Thus the critical depth of the potential well of the impurity on exceeding which a mode localized on the impurity is generated is dependent on the distance of the impurity from the surface (see Fig. 3.5) and varies from $c=0$ (bulk situation – the impurity is infinitely far from the surface) to $c=1$ (the impurity is located on the surface).

The depth of the impurity potential well for the generation of an antisymmetric localized mode is even greater. The critical value for these modes amounts to $c_{crit}=1/(N+1)+1/\Delta$, where Δ is the distance (in lattice units) from the impurity to the centre of the chain. The presence of the correction $1/\Delta$ in the critical condition

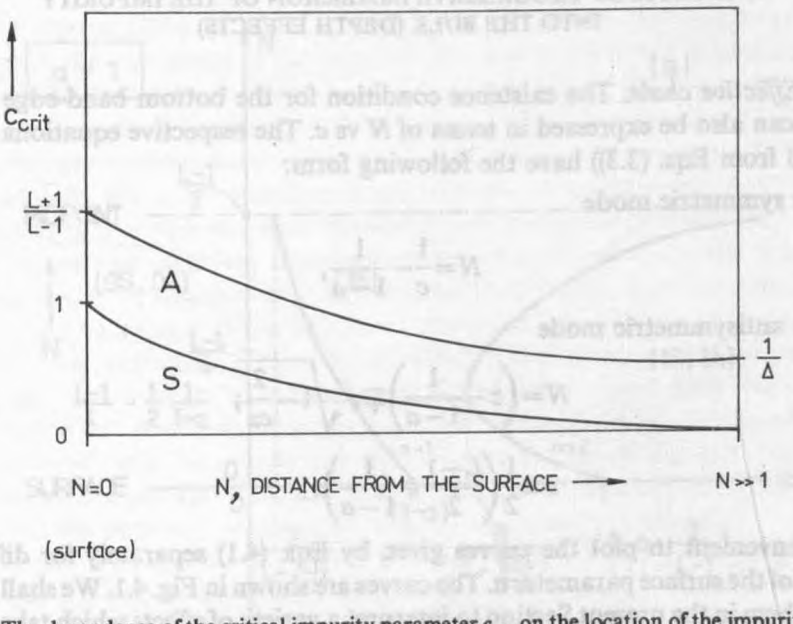


Fig. 3.5. The dependence of the critical impurity parameter c_{crit} on the location of the impurity in the chain; the surface parameter is assumed to be equal to zero ($a=0$). S(A) denotes a symmetrical (antisymmetrical) mode.

is due to the fact that the impurity has to "overcome" the delocalizing influence of the centre of symmetry.

Let us furthermore note that a perturbation on the surface (the assumption of $a \neq 0$) affects the critical condition for the impurity but insignificantly (see Fig. 3.1): if $a \to -\infty$ then $c_{crit} \to 1/N$, which differs but insignificantly from the value found above for the natural surface (the correction being of order $1/N^2$).

Let us now consider the inverse process, i.e., how the impurity modifies the critical condition for the generation of a surface mode. For an impurity of the "barrier" type ($c<0$) the critical value a_{crit} is raised; the correction does not exceed the term $1/N$; and the value $a_{crit}=1+1/N$ is obtained for $c \to -\infty$. Hence we draw the conclusion that the surface critical condition is more sensitive to the magnitude of the impurity potential than is the critical impurity condition to the surface potential: in the former case the correction is $1/N$-order, whereas in the latter it is $1/N^2$-order.

All in all, when it comes to the critical condition for the generation of surface and impurity modes, the surface and the impurity "feel" their presence mutually. But whereas the surface condition is primarily sensitive to the magnitude of the impurity potential (and less so to the distance between the surface and the impurity), the impurity condition is in the first place sensitive to the distance from the impurity to the surface (and less sensitive to the surface potential).

4. EFFECTS OF PROGRESSIVE IMMERSION OF THE IMPURITY INTO THE BULK (DEPTH EFFECTS)

1. *Effective chain.* The existence condition for the bottom band-edge mode ($k=0$) can also be expressed in terms of N vs c. The respective equations (to be derived from Eqs. (3.3)) have the following form:

for the symmetric mode

$$N=\frac{1}{c}-\frac{1}{1-a}, \tag{4.1a}$$

for the antisymmetric mode

$$N=\left(z-\frac{1}{1-a}\right)\mp z\sqrt{1-\frac{2}{cz}}; \tag{4.1b}$$

$$z\equiv\frac{1}{2}\left(\frac{L-1}{2}+\frac{1}{1-a}\right). \tag{4.2}$$

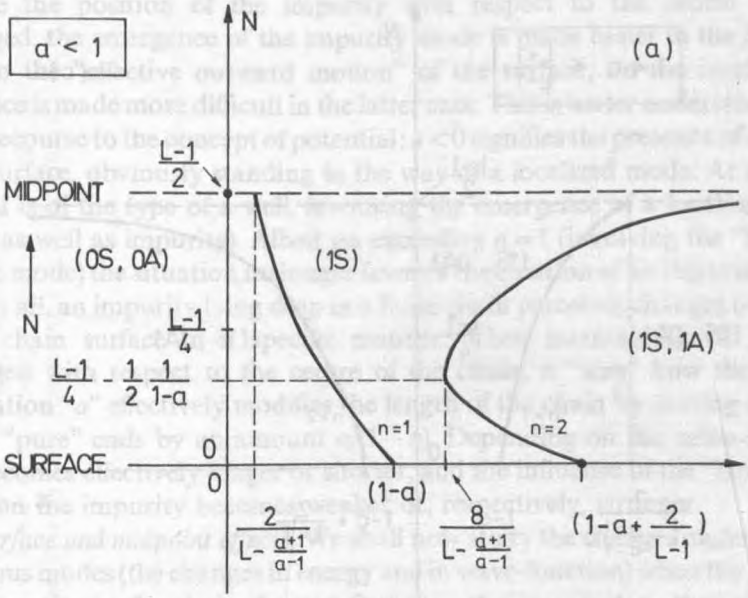
It is convenient to plot the curves given by Eqs. (4.1) separately for different ranges of the surface parameter a. The curves are shown in Fig. 4.1. We shall make use of them in the present Section to interpret a variety of effects which take place as the location N of the impurity changes.

First, however, we wish to draw attention to an interesting property of the Eqs. (4.1). It becomes apparent if one starts by writing them for $a=0$ (for a chain with unperturbed surface) and proceeds to a comparison with their general form for $a\neq 0$. Clearly, the Eqs. (4.1) with $a\neq 0$ reduce to those of the unperturbed chain if we introduce the following effective quantities:

$$N_{eff}=N+\frac{a}{1-a}, \tag{4.3a}$$

$$L_{eff}=L+\frac{2a}{1-a}. \tag{4.3b}$$

The transformation (4.3) tells us how the impurity "experiences" the perturbed surface ($a\neq 0$) compared with the unperturbed surface ($a=0$): the impurity "perceives" no difference between the two provided that the length of the chain with perturbed surface is subjected to a modification, leaving unchanged the position of the impurity with respect to the centre of the chain. Formally, the transformations (4.3) "remove" the perturbations from the surface into the bulk of the chain: the impurity now "perceives" the perturbed chain as an effective unperturbed chain of modified length equivalent to the initial perturbed chain. Thus, we have two cases: (i) the effective length of the chain exceeds its real length if $0<a<1$, whereas (ii) it is shorter than its real length for all other values of a.


a < 1
(a)
N
MIDPOINT
(0S, 0A)
(1S)
(1S, 1A)
SURFACE
n=1
n=2
c
0
(1-a)
a = 1
(b)
(0S, 0A)
(1S)
(1S, 1A)
n=1
n=2
0
c

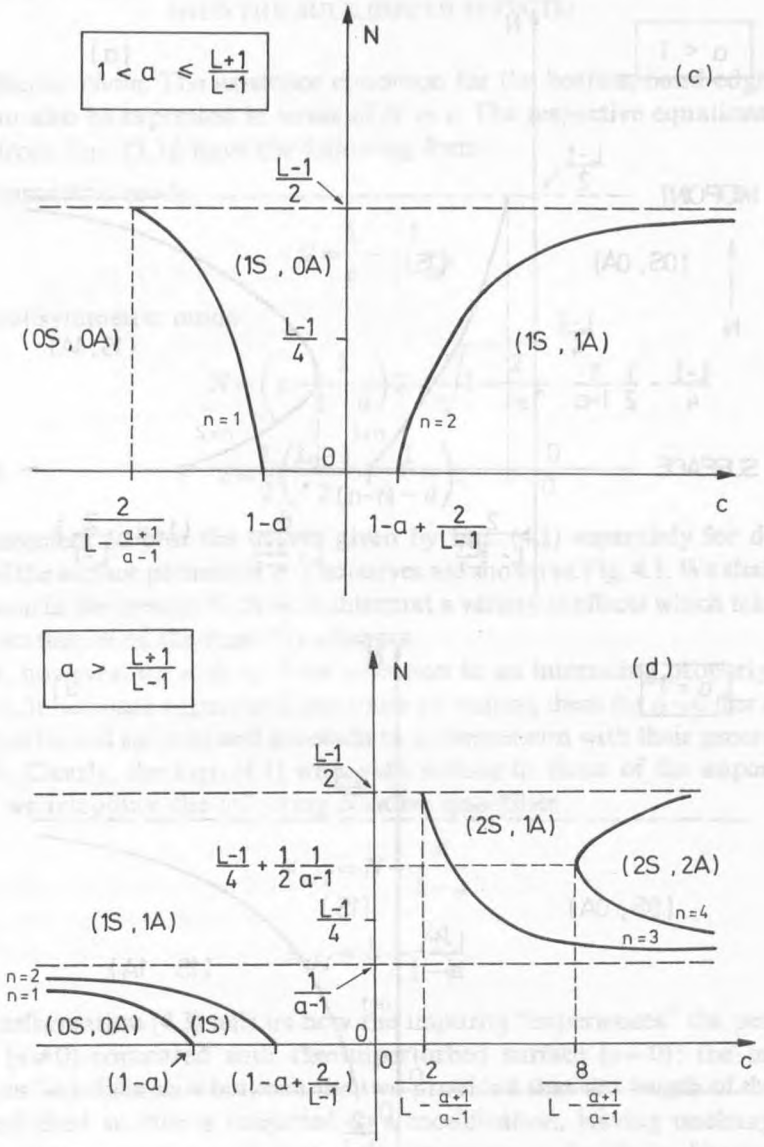


Fig. 4.1. Existence conditions (schematically) for LB modes in the N–c plane for different ranges of the surface parameter a. The chain of L atoms contains two impurity atoms, symmetrically disposed with regard to the chain center, at a distance of N atomic units from either surface of the chain (C is the implurity parameter). The curves marked $n=1, 3$ correspond to the existence conditions of the $k=0$ symmetric band-edge, whereas thise for $n=2, 4$ to $k=0$ antisymmetric ones. The plane splits into regions (mS, nA) where m symmetric and n antissymmetric LB modes exist simultaneously.

Since the position of the impurity with respect to the centre remains unchanged, the emergence of the impurity mode is made easier in the first case owing to the "effective outward motion" of the surface; on the contrary, its emergence is made more difficult in the latter case. This is better understood when having recourse to the concept of potential: $a<0$ signifies the presence of a barrier on the surface, obviously standing in the way of a localized mode. At $a>0$ the potential is of the type of a well, favouring the emergence of a localized mode (surface as well as impurity). Albeit on exceeding $a=1$ (involving the "birth" of a surface mode) the situation no longer favours the creation of an impurity mode.

All in all, an impurity lying deep in a finite chain perceives changes occurring on the chain surface in a specific manner: when maintaining its position unchanged with respect to the centre of the chain, it "sees" how the surface perturbation "a" effectively modifies the length of the chain by shifting either of the two "pure" ends by an amount $a/(1-a)$. Depending on the value of a, the chain becomes effectively longer or shorter, and the influence of the "perturbed" surface on the impurity becomes weaker or, respectively, stronger.

2. *Surface and midpoint effects.* We shall now study the changes undergone by the various modes (the changes in energy and in wave-function) when the position of the impurity in the chain changes (but the other parameters, thus the chain length $L=21$, the surface parameter a, and the impurity parameter c remain unchanged.) To begin with, we consider the unperturbed chain, $a=0$. Fig. 4.2a shows the changes in energy of the two lowest-lying modes ($n=1$; 2) as the impurity $c=1$ wanders away from the surface towards the midpoint of the chain, whereas Figs. 4.2b,c show the changes in profile of those modes in the "process of migration". When the impurity leaves the surface the two states sink below the bands becoming impurity localized modes (the one symmetric and the other antisymmetric); at first, their energies are degenerate, but as they approach the centre of the chain the levels split; the energy of the symmetric mode continues to decrease (i.e. this mode enhances its localization on the impurity), whereas the antisymmetric mode attains its strongest localization at about $N=5$, raises its energy approaching the band, and finally – on attaining the chain midpoint – sinks completely into the band thus becoming a bulk mode again. This enables us to distinguish three regions of sensitivity of the mode energy to changes in N: (1) in the near-surface region the localization of the two modes increases strongly due to the circumstance that the impurity abruptly frees itself of the delocalizing influence of the surface; (2) in the near-midpoint region also strong changes in localization of the modes take place: while the antisymmetric mode delocalizes, the symmetric mode dramatically lowers its energy; this behaviour is the result of the delocalizing influence exerted by the midpoint on the antisymmetric mode; (3) these two regions are separated by a region of stable localization (constant energy), which obviously assumes the shape of a plateau for greater values $|c|$ of the impurity parameter (see Fig. 4.3). This pattern is typical for impurity modes

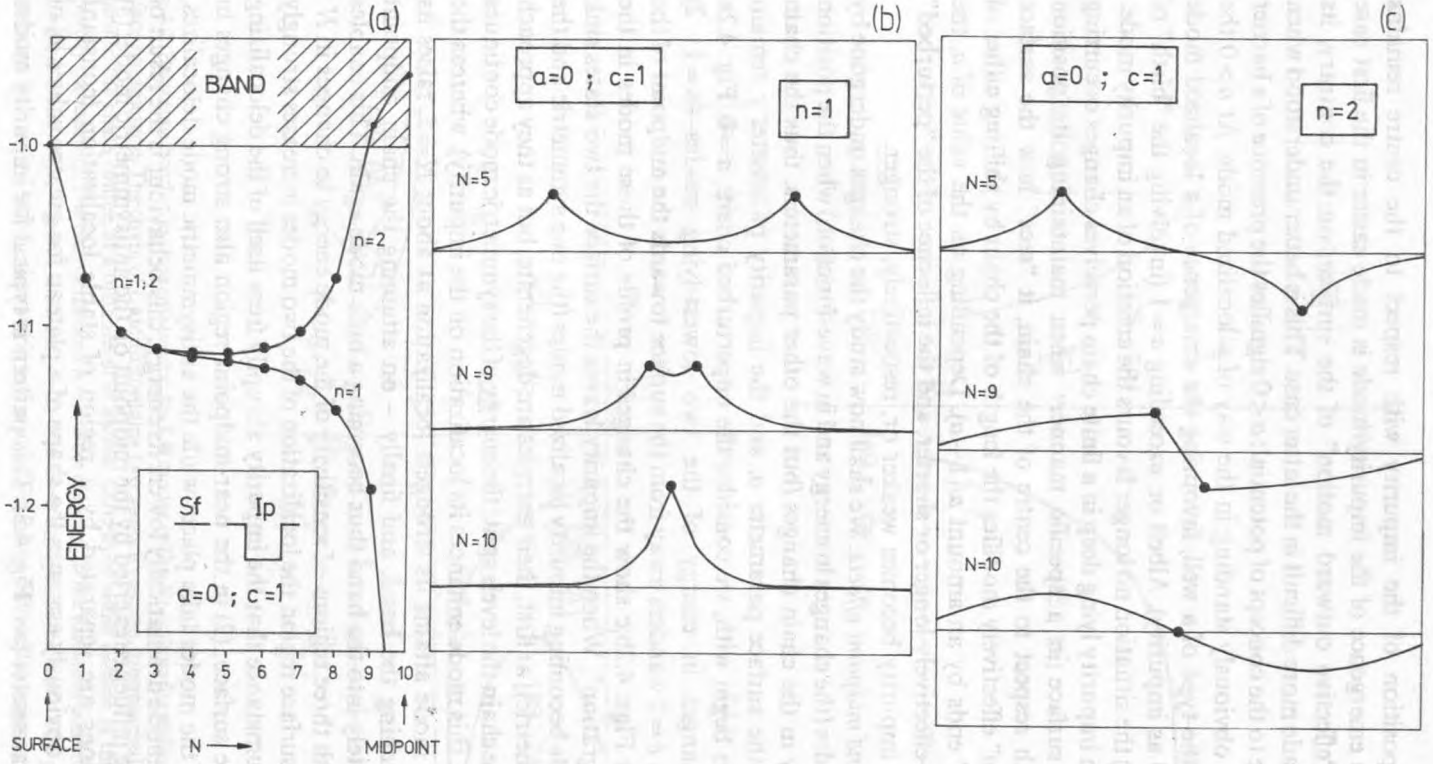


Fig. 4.2. (a) The reduced energy of modes with lowest n vs the position N of the impurity in the chain. One should refer each particular value of N to the corresponding chain shown in Fig. 2.1. Here, one has the opportunity to follow the energy of the respective modes by "sweeping" (by varying N) one by one all the chains shown in Fig. 2.1. Bold circles indicate IpM. Surface parameter $a=0$ (bulk potential), impurity parameter $c=1$ (potential well).

(b, c) Profiles of modes $n=1, 2$ shown for various N indicate increasing localization for the symmetric mode and delocalization of the antisymmetric mode with increasing N. Note the intrinsic analogy of these profiles with the bonding and antibonding curves for e.g. two hydrogen atoms.

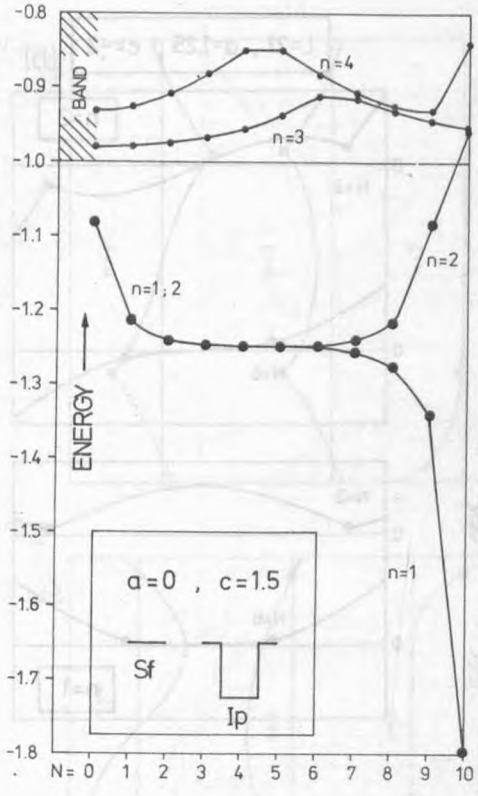


Fig. 4.3. Energy patterns (as in Fig. 4.2a) for $a=0$, $c=1.5$.

irrespective of whether they lie below or above the band (Fig. 4.4a shows the pattern for the two highest modes, L A); in all cases, it presents a "surface effect", a plateau, and a "midpoint effect".

Things proceed otherwise if the changes in N are accompanied by the "birth" of surface modes. This is shown in Fig. 4.4a, where on exceeding $N=4$ the two energy levels descend below the band becoming surface-localized modes (see also Fig. 4.4b). The two energy levels are practically totally degenerate and maintain their degeneracy to the end of the impurity's migration; beyond some position N, they become practically insensitive to its migration. Accordingly, in the N-dependence of the surface-mode energy, we distinguish two regions only: a "surface-effect" region, and a plateau. The nature of the changes in localization within the near-surface region hinges on the sign at c. If $c<0$ (Fig. 4.4), SfM localization increases with increasing distance of the impurity from the surface, and if $c>0$ the localization diminishes (Fig. 4.5).

All in all, the energy of the localized modes is sensitive to changes in position of the impurity in the chain; however, the consequences of this fact differ according to the position of the impurity with respect to the surface and midpoint and in accordance with the type of mode under consideration. As the impurity moves away from the surface but as long as it is still near the latter ("surface effect"), drastic changes take place in the localization of the modes – changes insensitive to the sign of c in the case of IpM modes, but sensitive thereto in that of SfM modes. As the impurity comes closer to the midpoint, changes in localization occur for IpM modes only ("midpoint effect") and the effect distinguishes between the mode symmetries delocalizing the antisymmetric modes and localizing the symmetric modes. Quite obviously, the SfM fails to "feel" the impurity if it is remote from the surface, whereas the IpM fails to "feel" changes in position of the impurity if the latter lies in the intermediate region where, already freed of the delocalizing influence of the surface, it has still not come under the delocalizing influence of the midpoint.

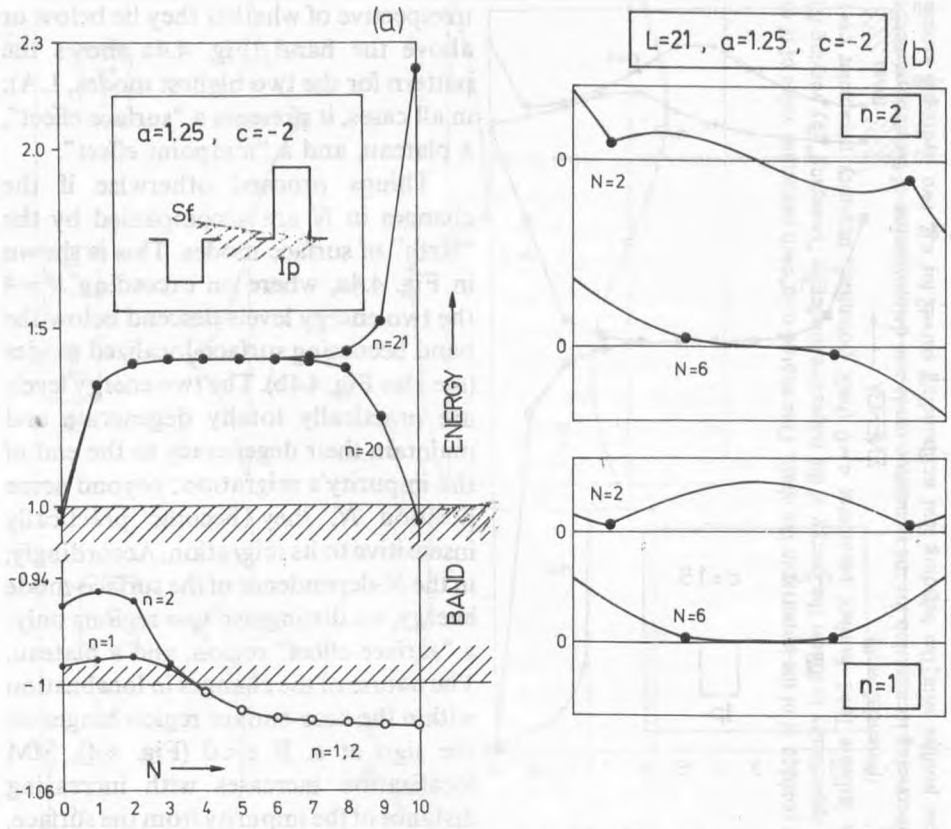


Fig. 4.4. (a) The reduced energy of modes with lowest ($n=1, 2$) and highest ($n=20, 21$) mode numbers versus the impurity location N. Full circles – IpM, void circles – SfM.
(b) The corresponding profiles of the modes $n=1, 2$; notice their increasing surface localization with increasing N.

3. *Energy patterns.* Localized modes arise as primary ($n=1, 2$) or secondary ($n=3, 4$). Impurity modes as well as surface modes can be created either as primary ones or as secondary ones. Fig. 4.2 shows impurity modes that are primary, whereas Fig. 4.5 shows impurity modes that are secondary. One readily notes that the behaviour "pattern" of the energy of impurity modes (versus growing N) does not depend on whether they are primary or secondary ones: the localization of the symmetric modes increases to become maximal in the midpoint, whereas that of the antisymmetric mode becomes maximal somewhere in the region between the surface and the midpoint. The surface modes too can be primary or secondary. Figs. 4.4 and 4.5 show them as primary; their E vs N pattern is dependent on the sign of the parameter c – their localization in the near-surface region can increase ($c<0$) or decrease ($c>0$). Secondary surface

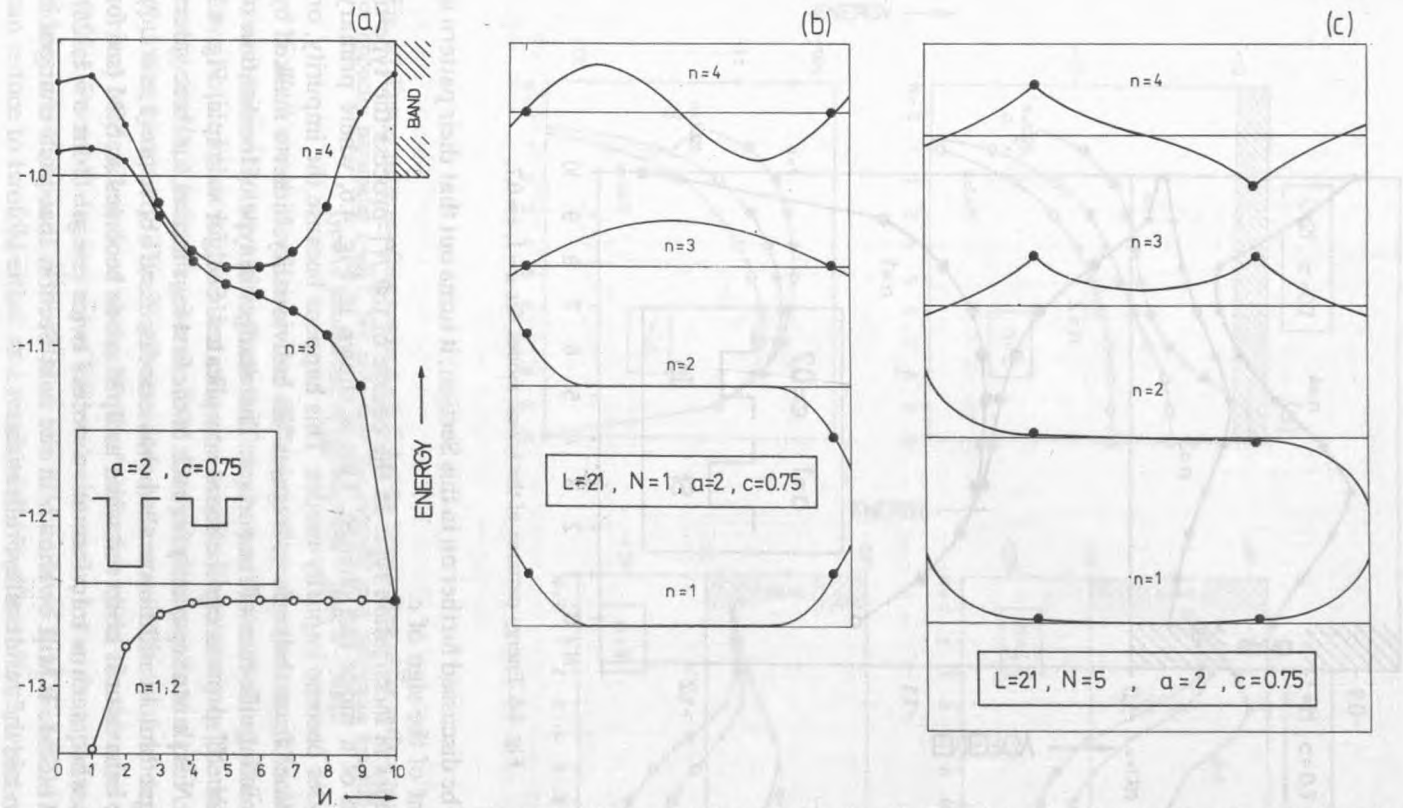


Fig. 4.5. (a) The reduced energy of the lowest modes ($n=1, 2, 3, 4$) versus the impurity location N in the chain. One should refer each particular value of N to the corresponding chain shown in Fig. 2.1. In other words, here one investigates the energy pattern of the respective modes when "sweeping" (by varying N) one by one all the chains of the set shown in Fig. 2.1. Full circles mean IpM, void circles – SfM. Surface parameter $a=2$ (deep well), impurity parameter $c=0.75$ (shallow well).

(b, c) Profiles of modes $n=1, 2, 3, 4$ for the same potential structure of the chain as in (a) and impurity location $N=1$ (b), $N=5$ (c).

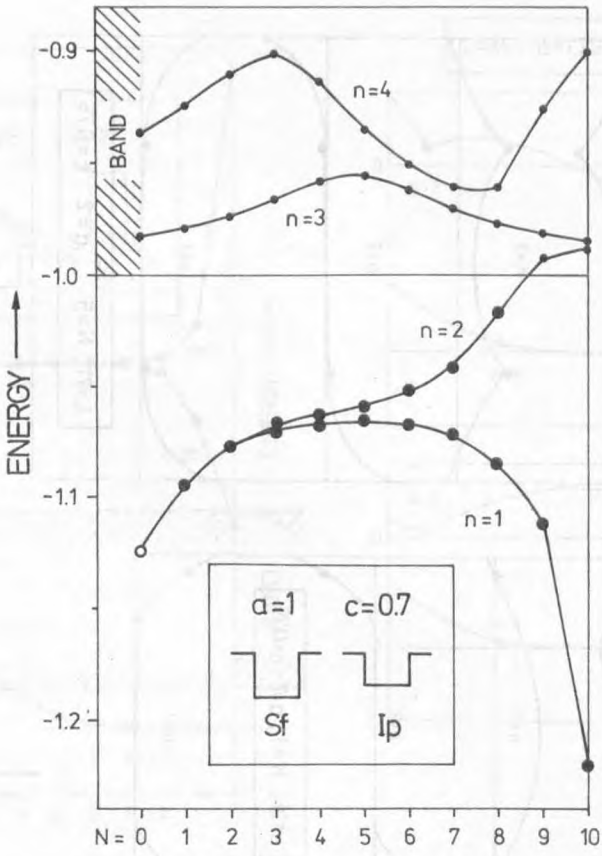


Fig. 4.6. Energy patterns of the lowest modes, for $a=1$, $c=0.7$.

modes will be discussed further on in this Section; it turns out that their pattern is independent of the sign of c.

4. *Changes in localization type.* In the course of the $N\uparrow$-process the type of localization of a mode can change. This is shown in Fig. 4.6, where primary surface modes become impurity-modes. This happens because the impurity, on its "separation" from the surface, "regains" its individuality, hitherto masked by the predominant influence of the surface. The changes in type of localization of modes in the $N\uparrow$-process can be more complicated. See, for example, Fig. 4.7 where E vs N is shown separately for each of the first four modes, for three values of the parameter a. In addition to the behaviour discussed above ($a=1$; $n=1, 2$), the inverse behaviour is observed when an IpM mode becomes an SfM (see for $n=3$), and when such a transformation occurs twice (see $n=2$ for $a=1.325$): SfM→IpM→SfM. It will be shown in the next Section that such changes in localization are the result of hybridization.

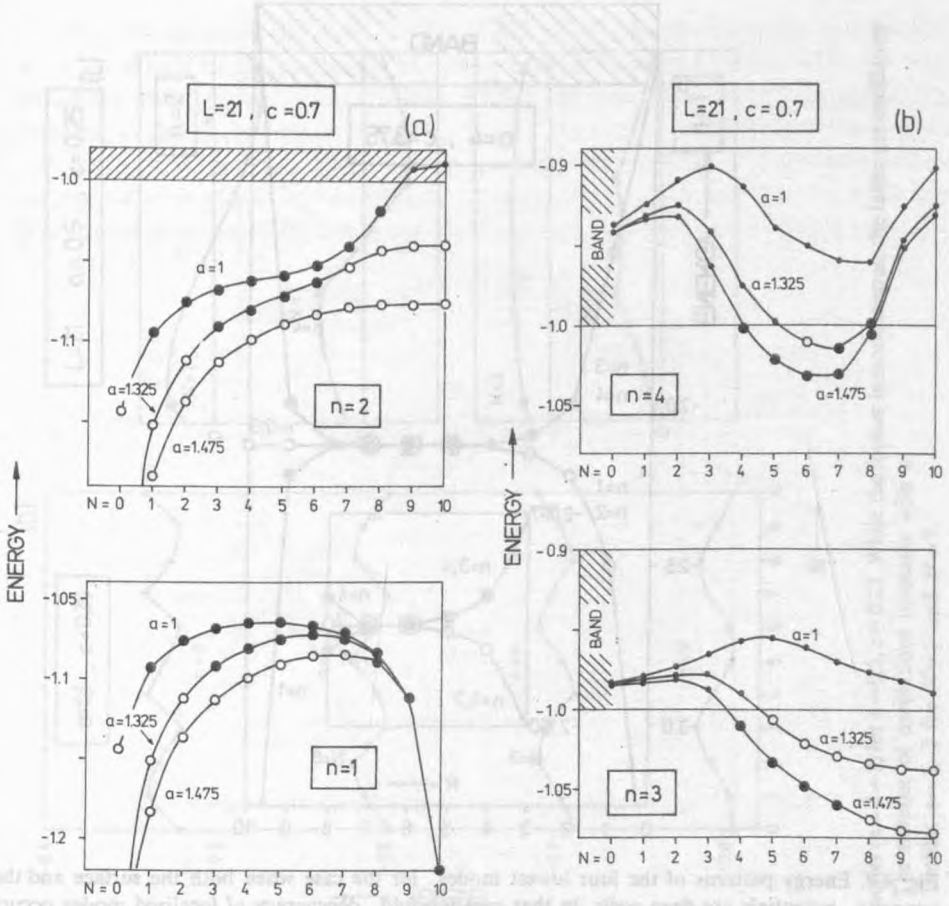


Fig. 4.7. Energy patterns of the modes $n=1, 2, 3, 4$ for three values of the surface parameter a and for impurity parameter $c=0.7$. We note how the increase in a influences the strength and the type of localization of the modes (• – Ipm, o – SfM).

5. *Bulk mode oscillations and LB degeneracy.* By the way, the N-process is accompanied by two more effects that may be worth mentioning. The reader may have noticed that high values of a or c lead to degeneracy in the localized LB energy levels; a twice degenerate level always corresponds to a pair of modes of opposite symmetry. The N-process does not remove the twofold degeneracy of surface modes, but does so due to the "midpoint effect" in the case of impurity modes. Fourfold degeneracy of LB levels can occur; for an example, see Fig. 4.8. If it does, it is composed of four states: two SfM and two IpM. Fourfold degeneracy can reduce to twofold either as a result of the "surface effect", which splits apart

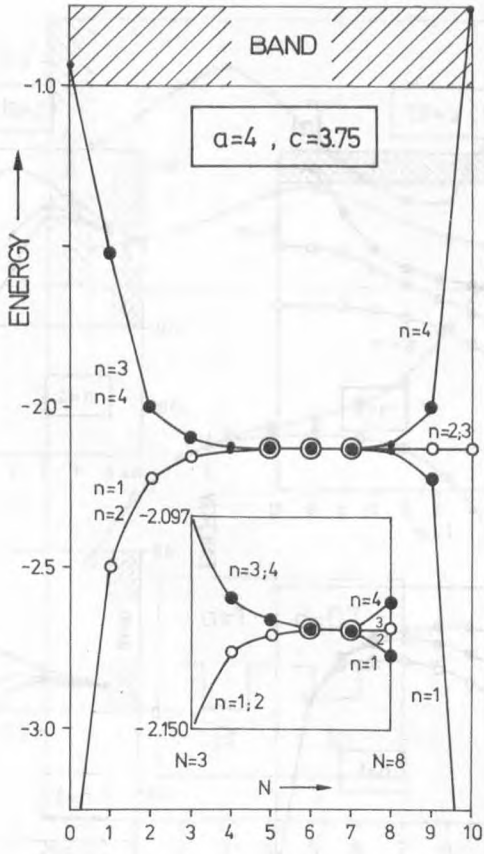


Fig. 4.8. Energy patterns of the four lowest modes for the case when both the surface and the impurity potentials are deep wells. In that case fourfold degeneracy of localized modes occurs (for impurity location $N=6, 7$).

states with different types of localization, or else by way of the "midpoint effect", which splits apart impurity of different symmetry.

We have seen that the energy of LB modes varied (almost) monotonically in the N-process. Now, it is a specific feature of bulk modes that they vary their energy oscillatorily in the N-process (see Fig. 4.9). The oscillations in energy increase for higher levels and are the greatest near the centre of the band, to decrease as the level approaches the upper edge of the band (Fig. 4.10). The oscillations of the bulk levels are obvious on grounds of perturbation calculus (Sec. 1), where the oscillations in energy reproduce the shape of the unperturbed wave-function whereas it will be kept in mind that the number of zeros in the profile of a mode increases as its energy approaches the centre of the band. Thus, there is a direct correspondence between Fig. 4.9 and Fig. 3.4, representing the profiles of unperturbed modes (cf. the case $A=0$).

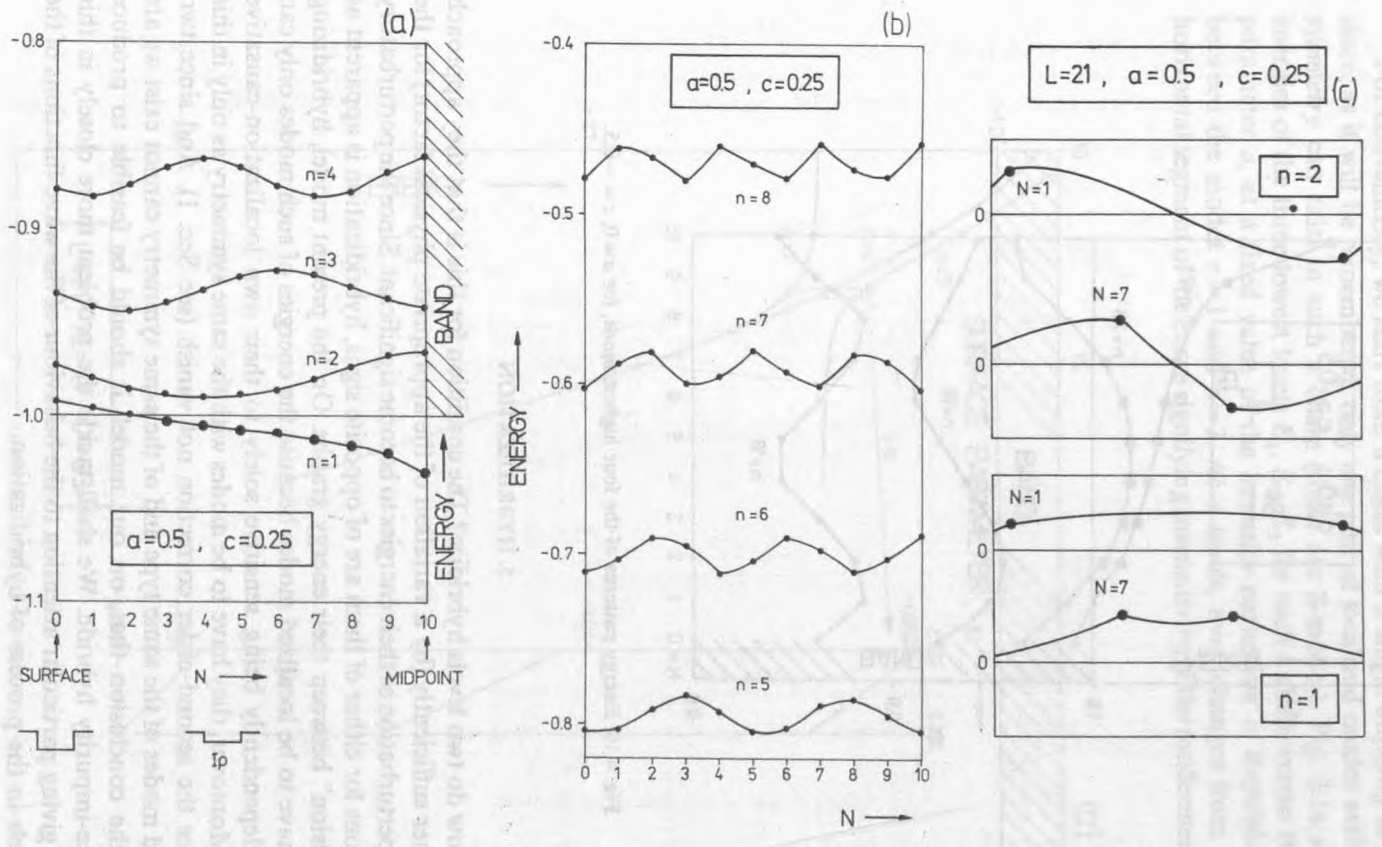


Fig. 4.9. (a, b) Energy patterns of IpM ($n=1$) and bulk modes ($n=2\div8$) for $a=0.5$, $c=0.25$. While the former is monotonous, the latter are oscillatory in shape. The number of oscillations increases with n.
(c) Profiles $n=1$, 2 for $N=1$ and $N=7$.

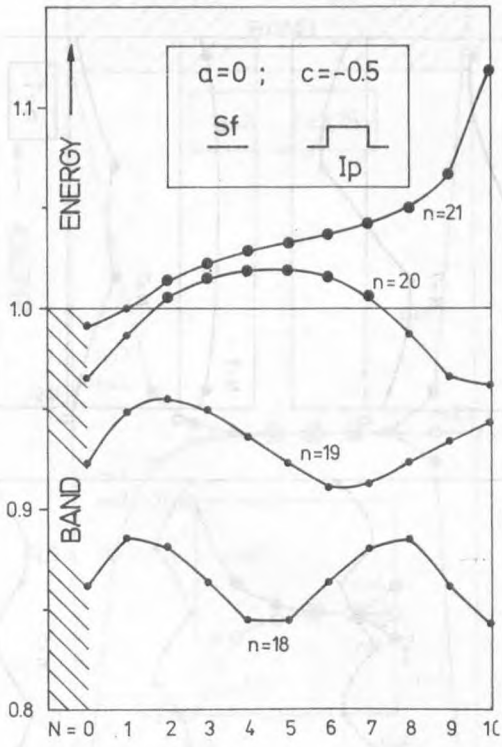
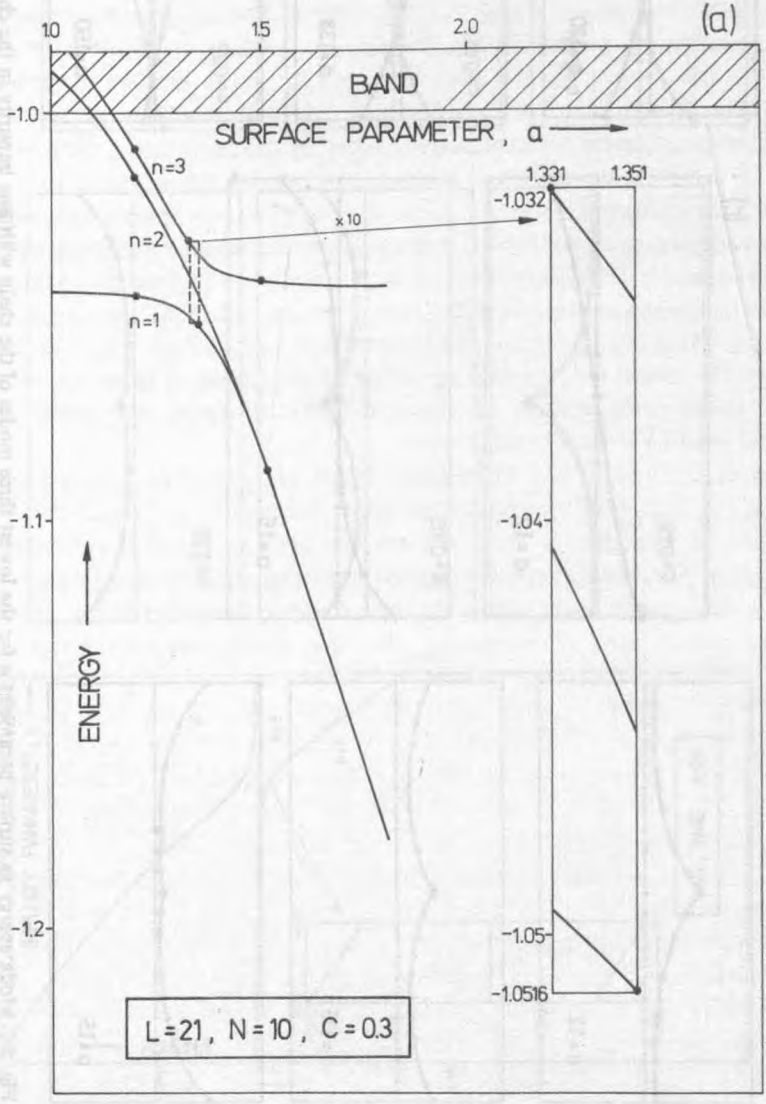


Fig. 4.10. Energy patterns of the four highest mods, for $a=0$, $c=-0.5$.

5. HYBRIDIZATION

1. How do two levels hybridize? The condition for this is that they approach each other sufficiently (by a variation of the appropriate physical factor) for the mutual perturbation of their energies to become significant. Since the perturbatory corrections for either of them are of opposite signs, hybridization is apparent as a "repulsion" between their energy graphs. On the present model, hybridizing modes have to be localized modes because the energies of such modes only can vary independently being sensitive solely to their own localization-causative factor. Moreover, they have to be modes with the same symmetry as only in this case does the second-order correction not vanish (see Sec. 1). And since two localized modes of the same type and of the same symmetry cannot exist we are led to the conclusion that, on our model, it should be feasible to produce a surface-impurity hybride. We shall tackle the problem more closely in this Section giving particular attention to the behaviour of the wave-functions of the two levels in the process of hybridization.

For conveniency, we start from a chain with a single impurity in its centre since, as it will be remembered, only *one* pair of localized modes *with the same symmetry* can exist in such a chain (these are S-modes). Fig. 5.1a shows the energies of the three lowest levels E_1, E_2, E_3 for such a chain versus the surface parameter a, at a fixed value of the impurity parameter c. Repulsion occurs between the modes $n=1$ and $n=3$. As a result, $n=1$ changes from IpM (the horizontal segment of the curve signifying insensitivity of the mode energy to the



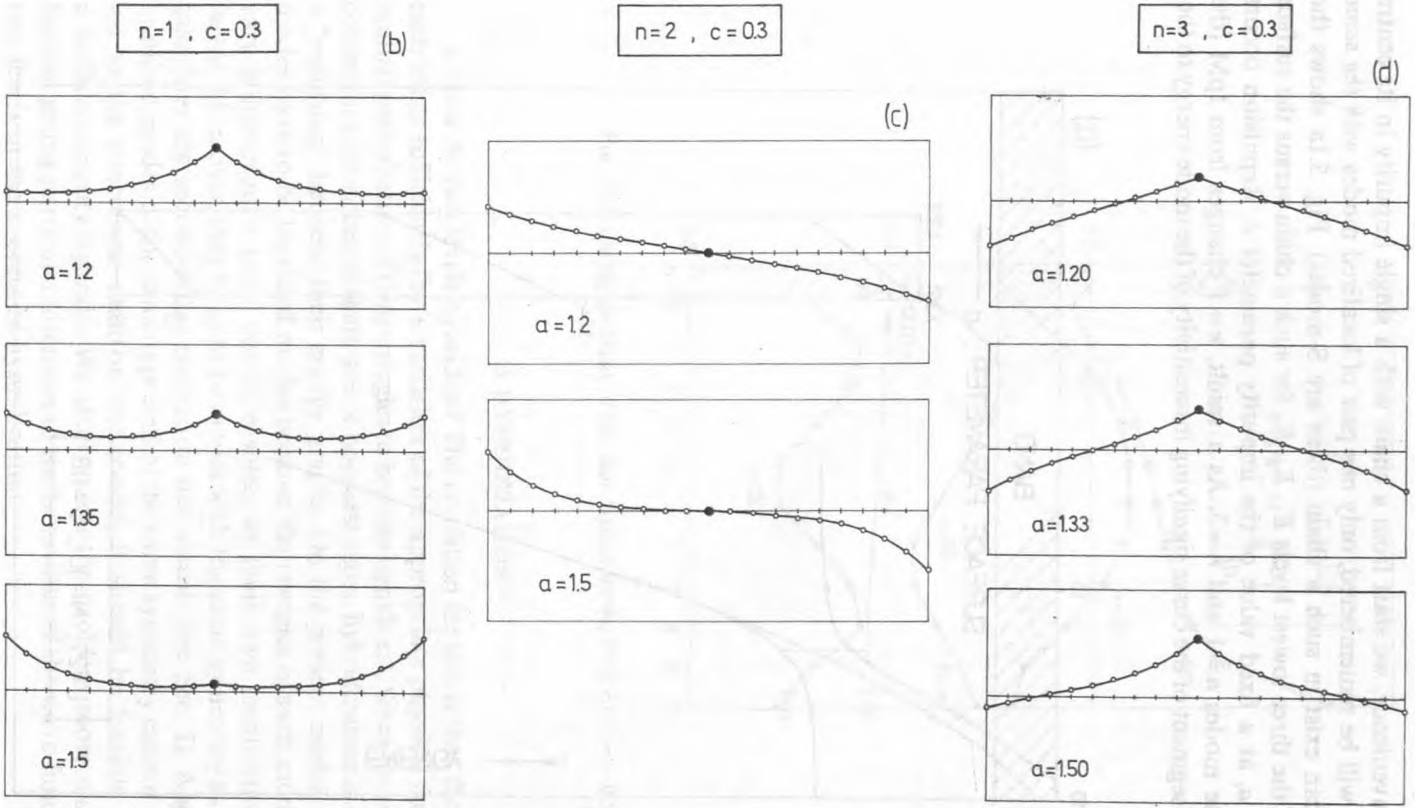


Fig. 5.1. Mode energy vs surface parameter a for the lowest three modes of the chain with one impurity in the chain centre (impurity parameter $c=0.3$). Graphs reveal the effect of hybridization of two symmetric LB modes $n=1$ and $n=3$. The inset shows the swapping rectangle, where the modes involved "swap" their surface-impurity localization. Shapes of the modes calculated for indicated points on the curves are shown separately; (b) $n=1$, (c) $n=2$; (d) $n=3$.

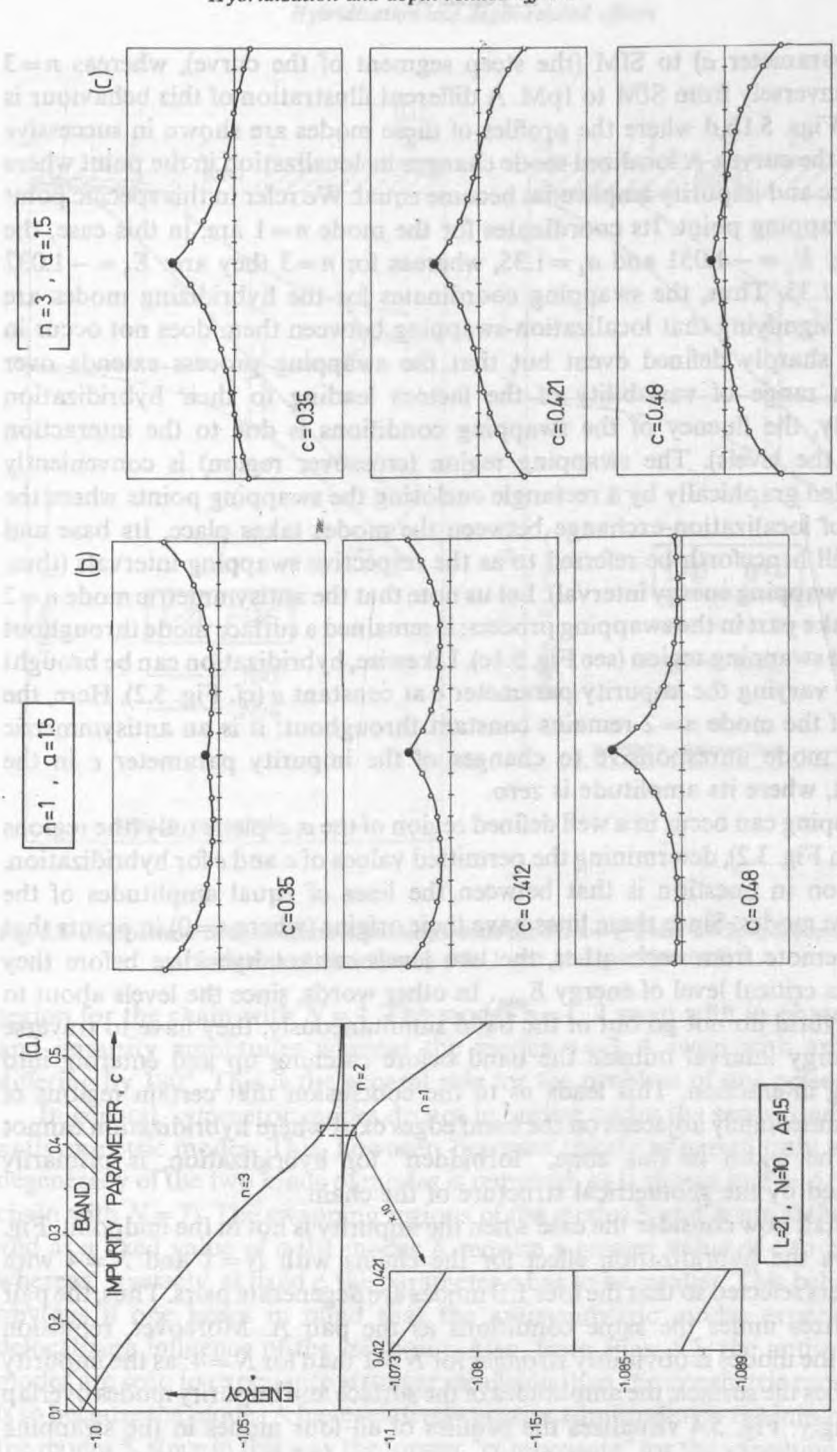


Fig. 5.2. Hybridization effect in the E vs c plane for a chain consisting of 21 atoms with the impurity in the centre. The surface parameter is kept constant at $a=1.5$; swapping between the modes $n=1$ and $n=3$ occurs within the interval $c\in(0.412–0.421)$ of the impurity parameter. Profiles of the modes (b) $n=1$ and (c) $n=3$ in the vicinity of the swapping region are shown separately.

surface parameter a) to SfM (the steep segment of the curve), whereas $n=3$ changes inversely from SfM to IpM. A different illustration of this behaviour is given in Figs. 5.1b,d where the profiles of these modes are shown in successive points of the curves. A localized mode changes its localization in the point where the surface and impurity amplitudes become equal. We refer to this specific point as the swapping point. Its coordinates for the mode $n=1$ are, in this case, the following: $E_1=-1.051$ and $a_1=1.35$, whereas for $n=3$ they are: $E_3=-1.032$ and $a_3=1.33$. Thus, the swapping coordinates for the hybridizing modes are different, signifying that localization-swapping between them does not occur in a single, sharply defined event but that the swapping process extends over a certain range of variability of the factors leading to their hybridization (obviously, the fluency of the swapping conditions is due to the interaction between the levels). The swapping region (crossover region) is conveniently represented graphically by a rectangle enclosing the swapping points where the process of localization-exchange between the modes takes place. Its base and height will henceforth be referred to as the respective swapping intervals (thus, e.g., the swapping energy interval). Let us note that the antisymmetric mode $n=2$ did not take part in the swapping process; it remained a surface mode throughout the whole swapping region (see Fig. 5.1c). Likewise, hybridization can be brought about by varying the impurity parameter c at constant a (cf. Fig. 5.2). Here, the energy of the mode $n=2$ remains constant throughout: it is an antisymmetric (surface) mode unresponsive to changes of the impurity parameter c in the midpoint, where its amplitude is zero.

Swapping can occur in a well defined region of the a, c-plane only (the regions shaded in Fig. 3.2), determining the permitted values of a and c for hybridization. The region in question is that between the lines of equal amplitudes of the respective modes. Since these lines have their origins (where $t=0$) in points that are far remote from each other, the two levels cannot hybridize before they traverse a critical level of energy $E_{\min}$. In other words, since the levels about to form a hybrid do not go out of the band simultaneously, they have to traverse some energy interval outside the band before catching up and entering into swapping interaction. This leads us to the conclusion that certain regions of energy immediately adjacent on the band edges exist where hybridization cannot occur. The width of this zone, "forbidden" for hybridization, is primarily determined by the geometrical structure of the chain.

We shall now consider the case when the impurity is not in the midpoint. Fig. 5.3 shows the hybridization effect for the chains with $N=1$ and $N=4$ with parameters selected so that the four LB modes are degenerate pairs. Thus, the pair S hybridizes under the same conditions as the pair A. Moreover, repulsion between the modes is obviously stronger for $N=1$ than for $N=4$: as the impurity approaches the surface, the amplitudes of the surface and impurity modes overlap increasingly. Fig. 5.4 visualizes the profiles of all four modes in the swapping

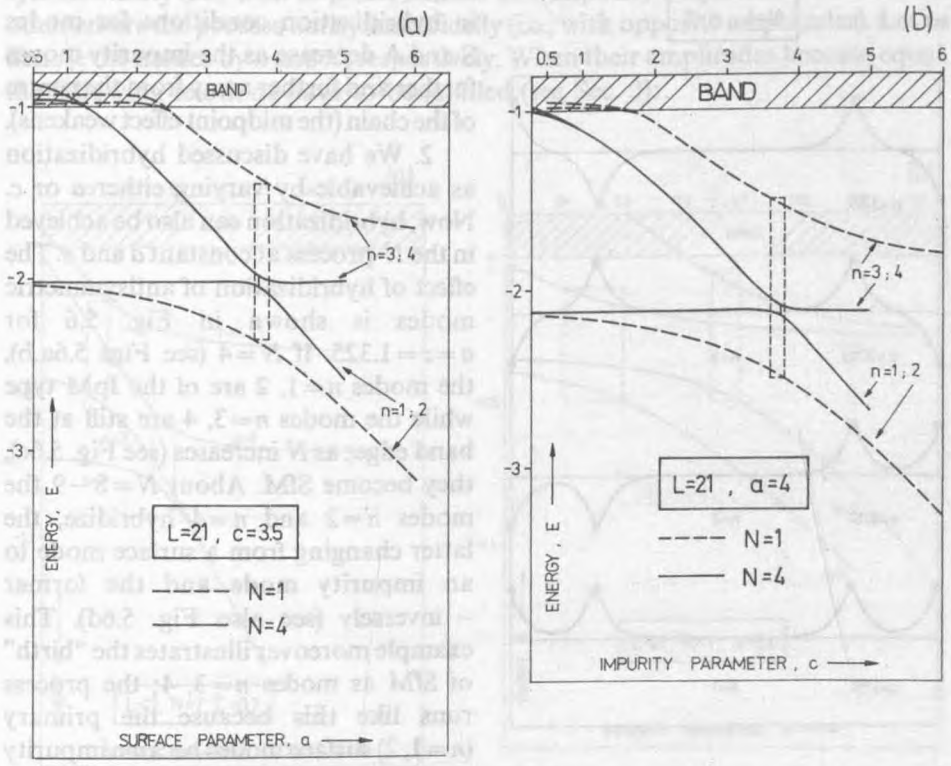


Fig. 5.3. Comparison of hybridization (for degenerate modes $n=1, 2$ and $n=3, 4$) occurring for two locations of the impurity ($N=1$ and $N=4$) in the chain.

region for the chain with $N=4$. The modes $n=1, 2$ swap with in-phase surface and impurity amplitudes whereas the modes $n=3, 4$ swap with amplitudes differing by 180°. This is the general rule for the problem of our present work.

In general, symmetric modes do not hybridize under the same conditions as antisymmetric modes. This, however, becomes clearly apparent only when the degeneracy of the two kinds of modes is removed, as is shown in Fig. 5.5 (for the chain with $N=7$). The swapping regions of the modes S and A are shifted apart, and at a fixed value of a the modes A require a greater value of c to hybridize whereas, inversely, at fixed c, the parameter a has to be smaller. This behaviour is obvious if one keeps in mind that the antisymmetric modes experience the delocalizing influence of the midpoint. Also, from Figs. 5.5, the antisymmetric modes are seen to experience stronger repulsion than the symmetric modes. This is so because the modes A have relatively greater amplitudes on the impurity than the modes S, since in this way the former "compensate" for the vanishing of their

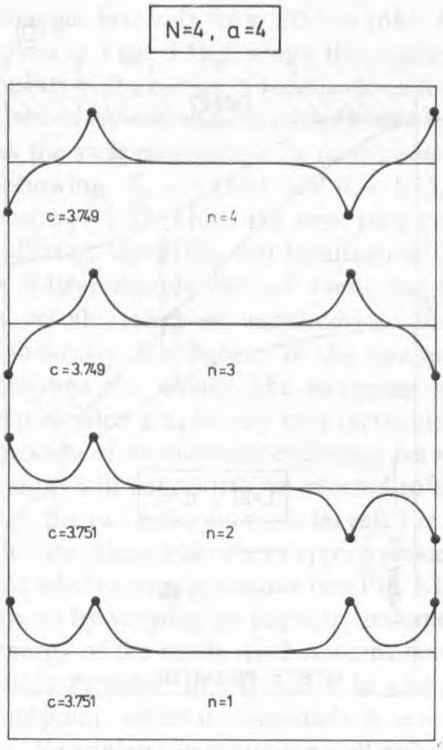


Fig. 5.4. Modes of Fig. 5.3b involved in hybridization.

amplitude in the midpoint. The differences in hybridization conditions for modes S and A decrease as the impurity moves further and further away from the centre of the chain (the midpoint effect weakens).

2. We have discussed hybridization as achievable by varying either a or c. Now, hybridization can also be achieved in the N-process at constant a and c. The effect of hybridization of antisymmetric modes is shown in Fig. 5.6 for $a=c=1.325$. If $N=4$ (see Figs 5.6a,b), the modes $n=1$, 2 are of the IpM type while the modes $n=3$, 4 are still at the band edge; as N increases (see Fig. 5.6c), they become SfM. About $N=8-9$ the modes $n=2$ and $n=4$ hybridize, the latter changing from a surface mode to an impurity mode and the former – inversely (see also Fig. 5.6d). This example moreover illustrates the "birth" of SfM as modes $n=3$, 4; the process runs like this because the primary ($n=1, 2$) surface modes became impurity modes sooner than the modes $n=3$, 4 left the band.

Hybridization of the symmetric modes $n=1$, 3 is shown in Fig. 5.7a for $a=1.475$ and $c=0.7$. The effect occurs at $N=7$. The profiles of the LB modes at $N=6$ are shown in Fig. 5.7b.

As mentioned above, hybridization is the reason why the modes involved change their localization twice in the course of the N-process. Fig. 5.8 shows E vs N for individual LB modes for two values of c and fixed a. Here, it is the mode $n=2$ that changes its localization twice, due to its interaction with the mode $n=4$. It is clear from a comparison of Fig. 5.8 and Fig. 4.7 that an increase in a (at fixed c) broadens the range of existence of the SfM, whereas an increase in c (at fixed a) broadens that of the IpM. From the physical viewpoint, this is obvious. However, it should be noted that in general both types of modes enhance their localization as the result of an increase in either a or c (obviously, to varying degrees).

3. With regard to the preceding discussion, it is time for an attempt at formulating some general theorems concerning hybridization. Let us consider the conditions for hybridization of surface and impurity modes. The two modes have to possess the same symmetry, and the one enters hybridizing swapping

symmetrically (i.e., with in-phase surface and impurity amplitudes) whereas the other enters the process antisymmetrically (i.e., with opposite amplitudes). Let us denote the modes by n and n', respectively. When their amplitudes become equal, the following relations have to be fulfilled (see Sec. 3):

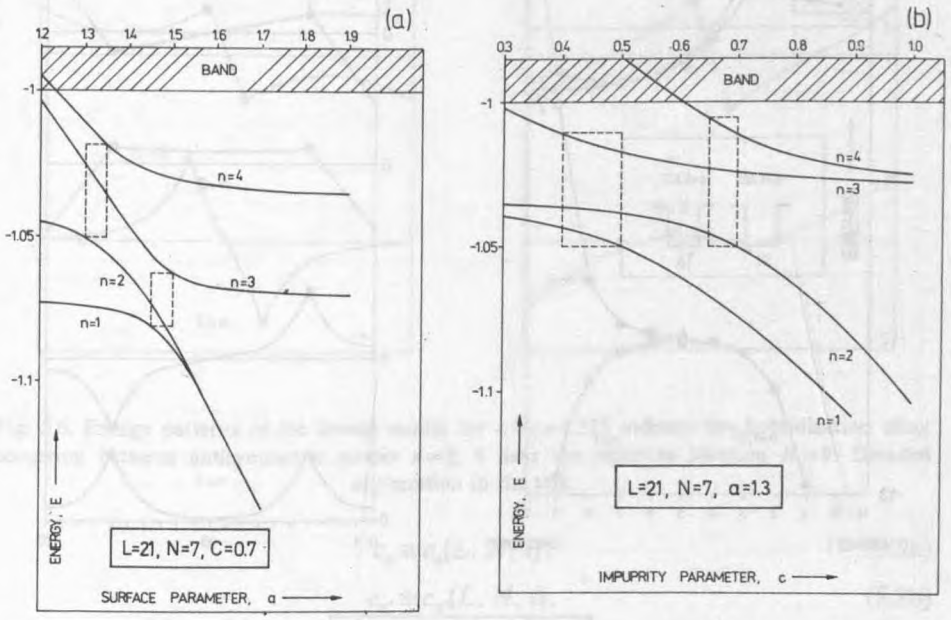
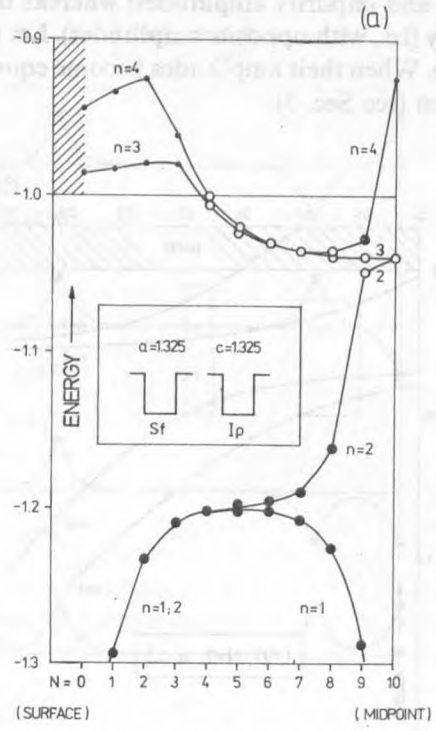


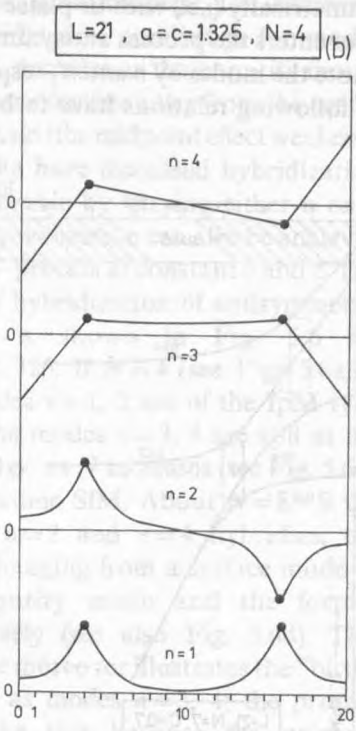
Fig. 5.5. Symmetric ($n=1$, 3) and antisymmetric ($n=2$, 4) modes hybridize separately.

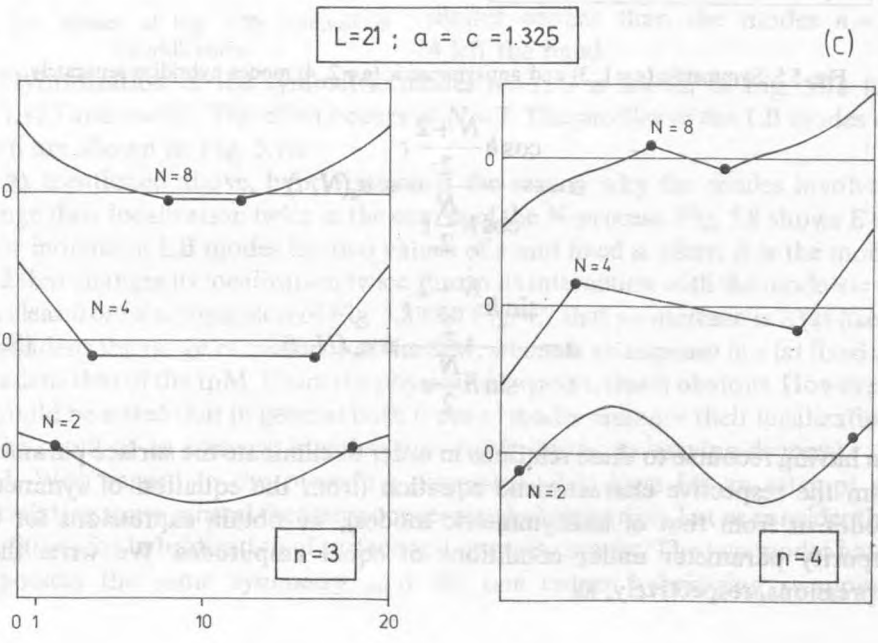
$$a=\frac{\cos h\dfrac{N+2}{2}t}{\cos h\dfrac{N}{2}t}\equiv a_n(N,t) \tag{5.1a}$$

$$a=\frac{\sin h\dfrac{N+2}{2}t}{\sin h\dfrac{N}{2}t}\equiv a_{n'}(N,t). \tag{5.1b}$$

On having recourse to these relations in order to eliminate the surface parameter from the respective characteristic equation (from the equation of symmetric modes or from that of antisymmetric modes), we obtain expressions for the impurity parameter under conditions of equal amplitudes. We write these expressions, respectively, as


(a)
-0.9
-1.0
-1.1
-1.2
-1.3
n=4
n=3
n=4
3
2
ENERGY
a=1.325
c=1.325
Sf
Ip
n=2
n=1;2
n=1
N = 0 1 2 3 4 5 6 7 8 9 10
(SURFACE)
(MIDPOINT)


L=21 , a=c=1.325 , N=4
(b)
n=4
n=3
n=2
n=1
0
0 1
10
20


L=21 ; a = c =1.325
(c)
N = 8
N = 4
N = 2
n=3
n=4
0
0 1
10
20

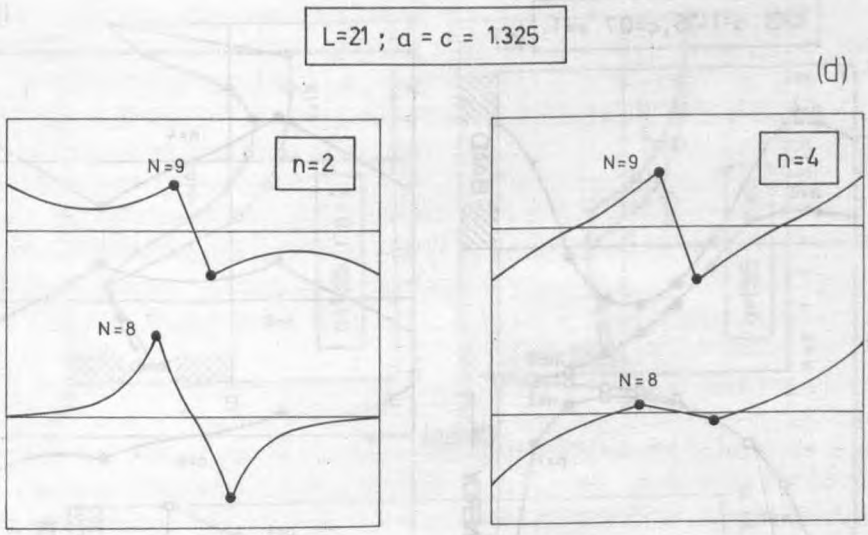


Fig. 5.6. Energy patterns of the lowest modes for $a=c=1.325$ indicate the hybridization effect occurring between antisymmetric modes $n=2$, 4 near the impurity location $N=9$. Detailed explanation in the text.

$$c_n \equiv c_n(L, N, t), \tag{5.2a}$$

$$c_{n'} \equiv c_{n'}(L, N, t). \tag{5.2b}$$

Hybridization of n and n' is achieved when the amplitudes of both modes become equal almost simultaneously (remember: the one in-phase, the other in opposite phase). This amounts to the fulfillment of the following approximate equalities:

$$a_n(N, t) \cong a_{n'}(N, t) \tag{5.3a}$$

$$c_n(L, N, t) \cong c_{n'}(L, N, t). \tag{5.3b}$$

These conditions can be achieved along a variety of paths depending on which of the initial parameters have been fixed. Before going any further, let us assume provisorically that the equalities (5.3) are fulfilled strictly. This, in fact, is a hypothetical situation since it amounts to neglecting the repulsion between the modes and to assuming their dispersion curves to intersect; the point of intersection would determine the energy level at which hybridization would occur. It is directly obvious from Eqs. (5.3) that the hybridization level (i.e., the value of t) is determined firstly by N from (5.3a), then by L from (5.3b), and ultimately by the values of a and c. Hence, each hybridization level requires "its own" chain, with completely defined structure of its geometry and potential. In practice, however, repulsion between the modes causes hybridization to occur in

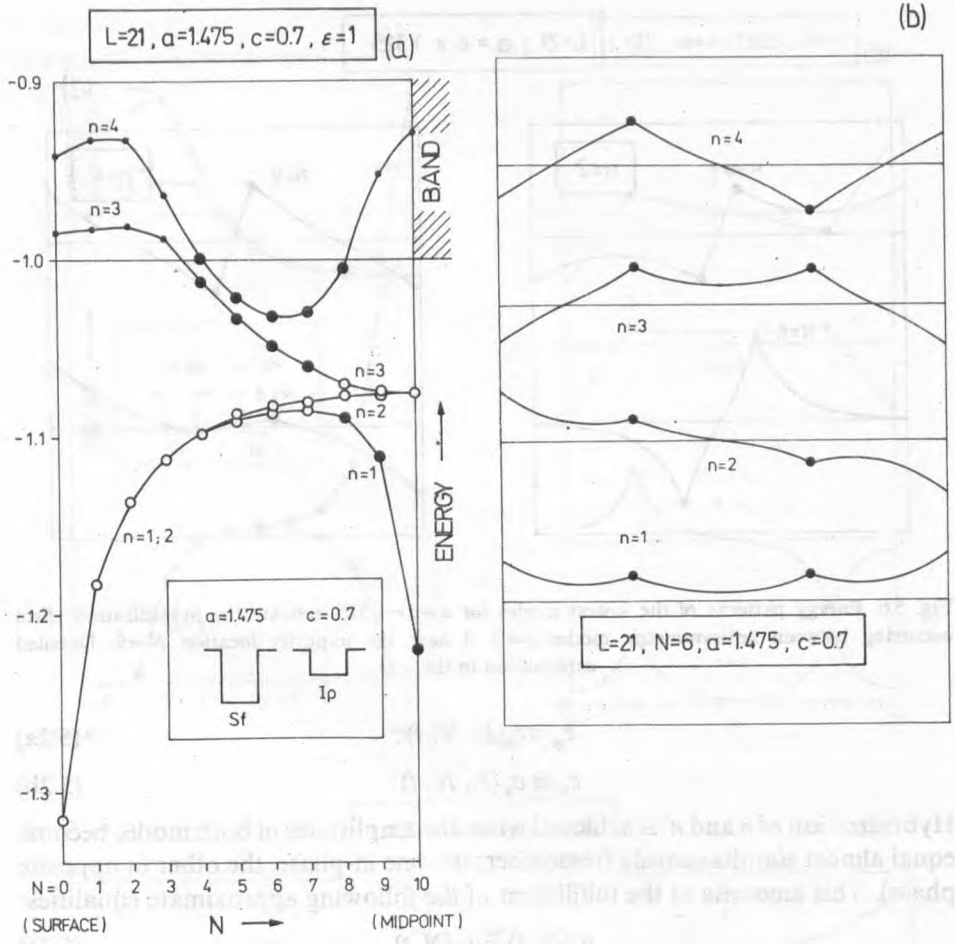


Fig. 5.7. Hybridization of symmetric modes $n=1, 3$.

a certain swapping energy *interval* rather than on a sharply defined swapping *level* . Now this implies that the structural parameters of the chain are also appropriately diffluent. In what follows we shall give some examples to illustrate our theorems.

First, consider the situation when the geometrical structure of the chain is fixed (L and N constant). The relation (5.1a) then leads to t as a function of a_n whence by (5.2a) we get

$$c_n = c_n(a_n). \tag{5.4a}$$

Similarly, from (5.1a) and (5.2a) we derive for the mode n'

$$c_{n'} = c_{n'}(a_{n'}). \tag{5.4b}$$

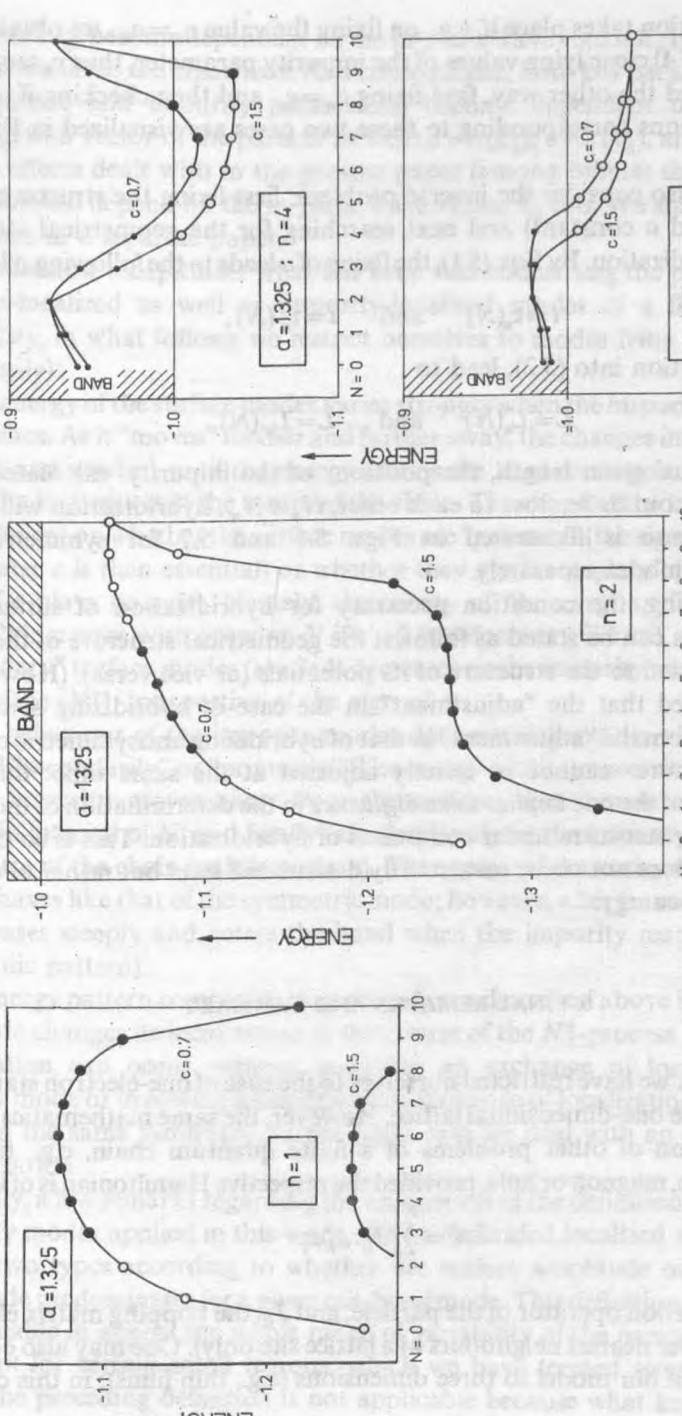


Fig. 5.8. Energy patterns of modes $n=(1\div4)$, for two impurity parameter values c and constant surface parameter a. Bold circles mean IpM, void ones – SiM.

Now hybridization takes place if, e.g., on fixing the value $a_n = a_{n'}$, we obtain from the equalities (5.4) close lying values of the impurity parameter, thus $c_n \approx c_{n'}$. One can also proceed the other way, first fixing $c_n = c_{n'}$ and then checking if $a_n \approx a_{n'}$. The hybridizations corresponding to these two cases are visualized in Figs. 5.1 and 5.2.

We could also consider the inverse problem: first fixing the structure of the potential (c and a constant) and next searching for the geometrical structure favouring hybridization. By Eqs. (5.1), the fixing of a leads to the following relations:

$$t = t_n(N) \quad \text{and} \quad t = t_{n'}(N), \tag{5.5a}$$

which, on insertion into (5.2), lead to

$$L = L_n(N) \quad \text{and} \quad L = L_{n'}(N). \tag{5.5b}$$

If, for a chain of given length, the positions of the impurity, calculated from Eqs. (5.5b) turn out to lie close to each other, $N_n \approx N_{n'}$, hybridization will occur. The phenomenon is illustrated in Figs. 5.6 and 5.7 for symmetric and antisymmetric modes separately.

In concluding, the condition necessary for hybridization of surface and impurity modes can be stated as follows: the geometrical structure of the chain has to be adjusted to the structure of its potentials (or vice versa). (However, it should be added that the "adjustment" in the case of hybridizing symmetric modes differs from the "adjustment" in that of hybridizing antisymmetric modes.) The two structures cannot be exactly adjusted at the same time: the exact determination of the one *implies some diffluence* in the determination of the other, complementary structure under conditions of hybridization. This is so because hybridization does not occur on a strictly determined level but rather in a given interval of the energy.

6. FINAL REMARKS AND SUMMARY

In our work we have restricted ourselves to the case of one-electron stationary states on a finite one-dimensional lattice. However, the same mathematics permit the investigation of other problems of a finite quantum chain, e.g., those of a single phonon, magnon or hole, provided the respective Hamiltonian is of the type

$$\hat{\mathcal{H}} = \sum_{l,l'} J_{ll'} \hat{a}_l^+ \hat{a}_{l'}. \tag{6.1}$$

with $\hat{a}_l^+$ the creation operator of the particle, and $J_{ll'}$ the hopping matrix elements (summation over nearest neighbours of a lattice site only). One may also consider the extension of our model to three dimensions (e.g., thin films); in this case the

quantities $J_{ll'}$ become dependent on the in-plane wave vector $k_{\|}$ lying in the plane perpendicular to the chain axis. As a consequence, both key parameters involved (the surface and impurity parameters) become dependent on the in-plane propagation vector of the particle as well: $a=a(k_{\|})$, $c=c(k_{\|})$, and consequently all the effects dealt with in the present paper (among others: the hybridization effect) should depend on the in-plane wave vector $k_{\|}$ too. We shall discuss these problems in a separate paper.

Let us now recapitulate what has been said concerning the properties of the surface-localized as well as impurity-localized modes of a finite chain (for simplicity, in what follows we restrict ourselves to modes lying below the bulk band only):

1. The energy of the surface modes varies strongly when the impurity recedes from the surface. As it "moves" further and further away, the changes in energy become weaker and weaker, until the energy attains the level corresponding to the case when the impurity is in the centre of the chain. The shape of the initial variations is dependent on whether the surface modes are "primary" (the sign of the impurity parameter c is then essential) or whether they are "secondary" (in this case the sign of c plays no role). Namely, the energy of "primary" surface modes (i.e., $n=1; 2$) increases with growing N if $c>0$ but decreases if $c<0$, whereas that of "secondary" surface modes ($n=3; 4$) decreases as the impurity moves away from the surface ($N\uparrow$), irrespective of the sign of c.

2. The behaviour of the impurity modes does not depend on whether they are created "secondarily" or "primarily". The energy of the symmetric IpM decreases as the impurity moves away from the surface, then becomes stable within a certain interval of N, and finally falls drastically as the impurity "approaches" the centre of the chain (saddle pattern). The energy of the antisymmetric IpM at first behaves like that of the symmetric mode; however, after traversing a plateau, it increases steeply and enters the band when the impurity reaches the centre (parabolic pattern).

3. An energy pattern combining the two patterns described above is evidence that the mode changes its localization in the course of the $N\uparrow$-process. The change in localization can occur without involving an exchange of localization with another mode or involving a simultaneous exchange of localization with another mode of the same symmetry. In the latter case we deal with an effect of mode hybridization.

4. Finally, a few remarks regarding the uniqueness of the definition of surface and impurity modes applied in this work. We have divided localized modes into the above two types according to whether the surface amplitude or the impurity amplitude predominates for a given out-band mode. This definition of localization is applicable in almost the whole range of variability of the parameters a, c and N except for certain small regions, which we have termed swapping regions, where the preceding definition is not applicable because what happens there is

a mutual exchange of localization between modes of the two types. The exchange, however, is by no means simultaneous: while one of the two modes has already won amplitudinal predominance in a given site of the chain, the other mode still retains amplitudinal predominance throughout a certain interval of the parameters. Thus, the swapping region is a region where the two modes compete for their localization and where the type of localization of a mode can be determined only by extrapolation from adjacent regions.

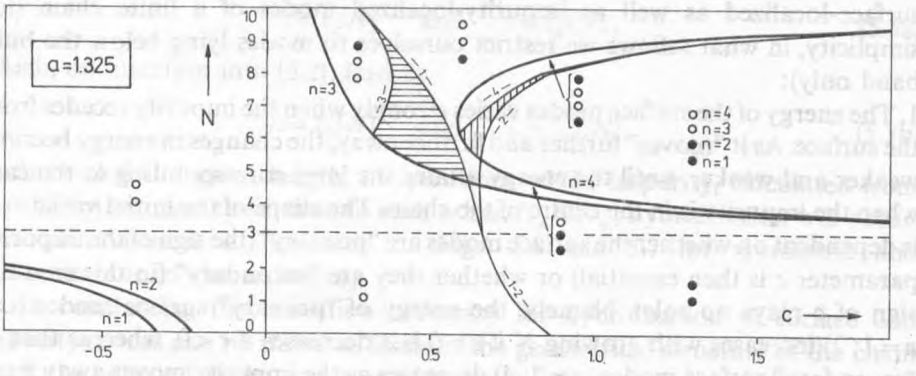


Fig. 6.1. The lines of equalized surface and impurity amplitudes, marked -*n*-for a mode *n*. The shaded areas represent swapping regions, respectively for symmetric modes (the region bounded by the lines -1- and -3-) and for antisymmetric modes (that bounded by the lines -2- and -4-). In the unshaded regions the localized modes have a uniquely determined type of localization (denoted as: o – SfM; ● – IpM), whereas in the swapping regions the localization of the respective modes is ambivalent.

The above is illustrated in Fig. 6.1, where the swapping regions are plotted in the N,c-plane. A localized mode, on "passing" through the relevant swapping region, changes the type of its localization. To the passage of a pair of modes with identical symmetry through the swapping region there corresponds an effect of their hybridization as the result of which the two modes exchange the types of their localization. If the swapping region is narrow, hybridization occurs sharply, but if it is broad then hybridization is diffluent. Everywhere (except in the swapping regions) our definition of the types of mode localization fulfills the requirement that one mode at the most shall be localized on a given perturbation.

The swapping regions are adjacent on the curves of "creation" of secondary modes (see Fig. 6.1). Accordingly, these curves are divided into three ranges: one where an SfM will be created, one where an IpM will arise, and a buffer range separating the two, where the type of the mode in creation is not uniquely defined (this is just the range on which the swapping region is adjacent). The "creation" curves of primary modes have no swapping range, and the two (IpM and SfM) intervals neighbour on each other directly.

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